HETEROCYCLES, Vol. 78, No.12 , 2009, pp. 3037 - 3051. © The Japan Institute of Heterocyclic Chemistry
Received, 26th August, 2009, Accepted, 17th September, 2009, Published online, 18th September, 2009
DOI: 10.3987/COM-09-11824

PREPARATION OF 1,4-BIS(3-ETHYNYLTHIENO[3,2-*b*]THIOPHEN-2-YL)BENZENE DERIVATIVES AS PEPTIDE-INSPIRED MOLECULES[1]

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Abstract – 1,4-Bis(3-ethynylthieno[3,2-*b*]thiophen-2-yl)benzene derivatives, as well as 1-(3-ethynylthieno[3,2-*b*]thiophen-2-yl)-4-(2-ethynyl-3-thienyl)benzene derivative and 2,5-bis(2-ethynyl-3-thienyl)thieno[3,2-*b*]thiophene derivative, containing thieno[3,2-*b*]thiophene moieties with pseudoaxis, was prepared and their UV-vis spectra were studied. Extension of π-system through the central aromatic ring was suggested by the UV-vis spectra.

INTRODUCTION

Bio-inspired or biomimetic artificial large molecular systems, including artificial molecular architecture, are of current interest.[2,3] On the other hand, heteroarene-based large molecular systems, such as oligothiophenes and polythiophenes, have attracted much interest in the fields of physical organic chemistry, materials science, and synthetic organic chemistry.[4,5] We previously reported the development of peptide-inspired spacers such as a 1,4-bis(2-ethynyl-3-thienyl)benzene spacer (Chart 1, abbreviated to the ETB spacer)[6] and a 4,4'-bis(2-ethynyl-3-thienyl)biphenyl spacer (ETAr spacer).[7] We have reported the related compounds such as **1a**–**d**,[6–8] an unsymmetrical compound **2**,[9] and a linked system **3**.[7] The ETB spacer is a promising and easily tunable spacer of three-ring system, which has a six-membered ring (1,4-phenylene moiety) and a pair of five-membered rings (3-thienyl moieties) at the both ends of the 1,4-phenylene axis. Rebek, Jr. and co-workers have independently reported an α-helix mimicking three-ring system **4**.[10] Hamilton and co-workers recently reported compound **5** and mentioned about the effectiveness of such 5-6-5 three-ring scaffold for α-helix mimetics.[11] Although polarity of the molecules and the directions of the side chains are different in these systems, our system, by tuning the side chains, may lead to the peptide-inspired large molecular systems.

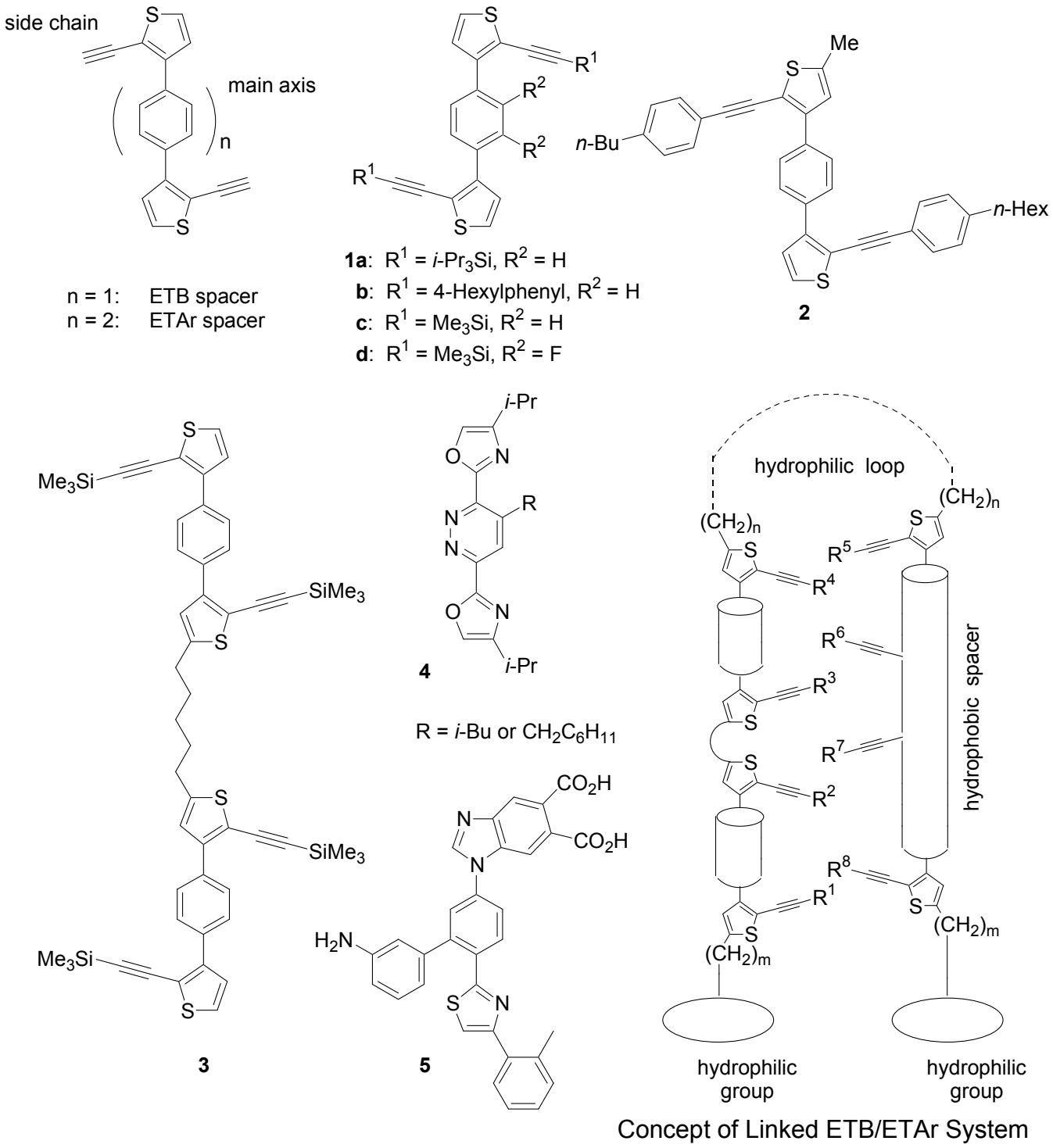


Chart 1

In order to progress the investigation of our ETB/ETAr spacer-linked systems (Chart 1), preparations of various molecular components including auxiliary spacers are desirable: Thieno[3,2-*b*]thiophen-2,5-diyl is one of versatile π-spacers[12] in materials science and it is often used with other spacers such as 1,4-phenylene, 2,5-thienylene, vinylene, and ethynylene. For our purpose, utilization of 3-*ethynyl*thieno[3,2-*b*]thiophen-2,5-diyl (**A** in Chart 2) is desirable, because it has an ethynyl side chain

and a pseudoaxis through the 2,5-positions[13] and it will work as an alternative spacer for the 2-ethynylthiophene moiety of the ETB/ETAr system. However, studies on 3-ethynylthieno[3,2-*b*]thiophenes or 1,4-bis(thieno[3,2-*b*]thiophene-2-yl)benzenes are limited.[14–20] We now report development of 3-ethynylthieno[3,2-*b*]thiophene derivatives **B** and **C** (Chart 2), containing the auxiliary π-spacers for our ETB/ETAr spacer-linked systems.[6–9] In addition, we describe here preparations of related compounds containing the structures **D** or **E**.

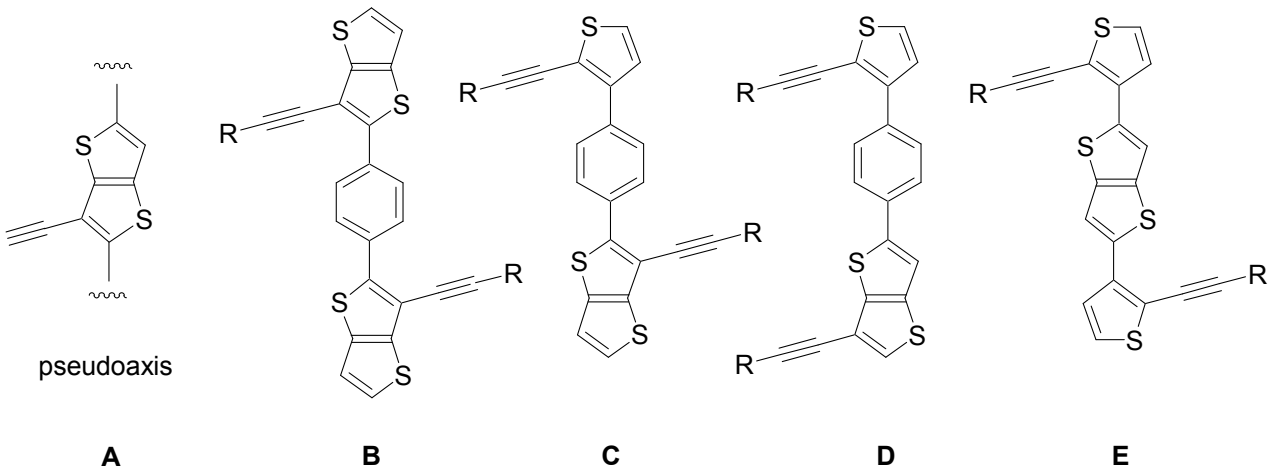
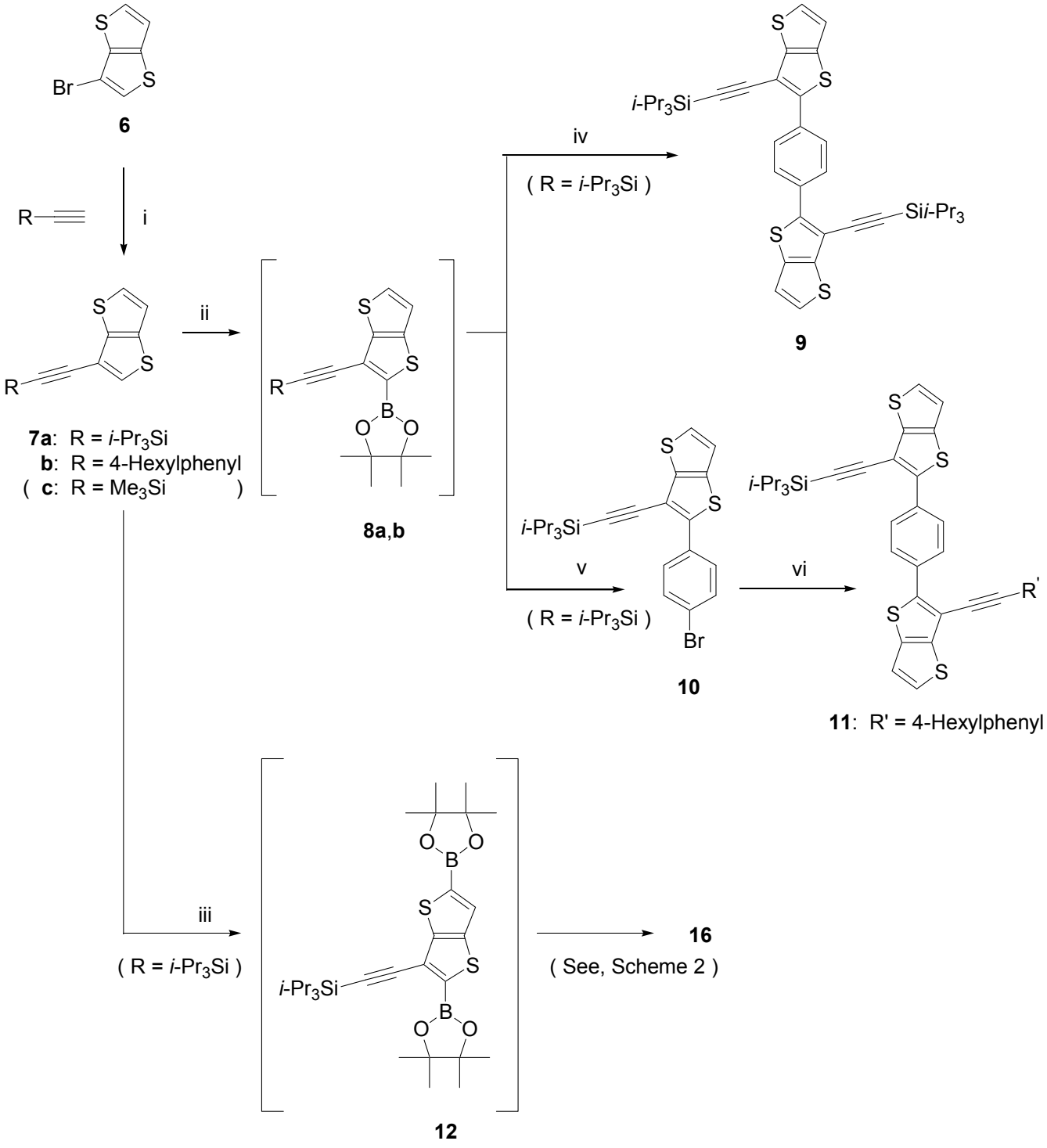


Chart 2

RESULTS AND DISCUSSION

3-[2-(Triisopropylsilyl)ethynyl]thieno[3,2-*b*]thiophene (**7a**) and 3-[2-(4-hexylphenyl)ethynyl]thieno-[3,2-*b*]thiophene (**7b**) were prepared by the Sonogashira cross coupling reaction of 3-bromothieno[3,2-*b*]thiophene (**6**)[21] with the corresponding alkynes in 97% and 87% yield, respectively (Scheme 1). Similarly, 3-[2-(trimethylsilyl)ethynyl]thieno[3,2-*b*]thiophene (**7c**) was prepared in 90% yield. Structures of the compounds **7a**,**b** can be regarded as alternatives for the 2-ethyny-3-thiophene structures in the ETB systems.

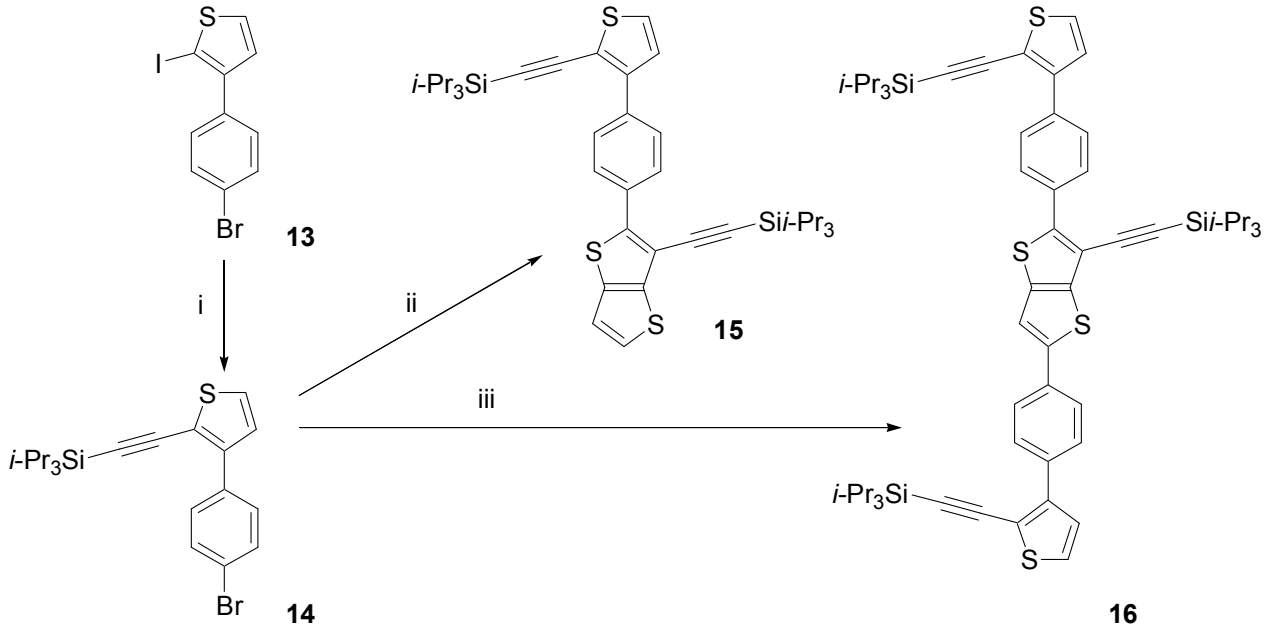
Utilization of compounds **7a**,**b** was performed as follows: Reaction of **7a** with butyllithium followed by treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded **8a** as a major product, along with some by-products such as **12** (see below). Suzuki-Miyaura cross coupling reaction of the crude **8a** with 1,4-diiodobenzene afforded a symmetrically substituted compound **9** in 13% yield (based on the starting **7a**). On the other hand, reaction of crude **8a** with 1-bromo-4-iodobenzene gave **10** (21% yield based on the starting **7a**), which was converted to an unsymmetrical derivative **11**, by a cross coupling reaction of **10** with **8b** (prepared from **7b**), in 62% yield (based on **10**).



Reagents and conditions: i, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, 1,4-dioxane or THF; ii, *n*-BuLi (ca. 1 equiv.), THF, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (ca. 1 equiv.); iii, *n*-BuLi (2 equiv.), THF, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 equiv.); iv, 1,4-diiodobenzene, $Pd(PPh_3)_4$, K_2CO_3, THF, toluene, H_2O; v, 1-bromo-4-iodobenzene, $Pd(PPh_3)_4$, K_2CO_3, THF, toluene, H_2O; vi, **8b**, $Pd(PPh_3)_4$, K_2CO_3, THF, toluene, H_2O.

Scheme 1

As for the preparation of compounds with structure **C** in Chart 2, 1-bromo-4-[2-(triisopropylsilylethynyl)-3-thienyl]benzene (**14**) was prepared from 1-bromo-4-(2-iodo-3-thienyl)benzene (**13**)[9] (Scheme 2). Suzuki-Miyaura cross coupling reaction of **14** with crude **8a** afforded (thieno[3,2-*b*]thiophen-2-yl)(3-thienyl)benzene derivative **15** in 21% yield (based on the starting **7a**, Scheme 1). In this reaction, compound **16** was also obtained (8% yield based on **7a**), because the crude starting material of **8a** contained **12** as mentioned above. When butyllithium (2 equiv.) was reacted with **7a** and the reaction mixture was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2 equiv.), compound **12** was formed as a major product (Scheme 1). A cross coupling reaction of **12** (containing a trace amount of **8a**) with **14** afforded **16** in 58% yield based on **7a**. It should be mentioned that compound **16** can be regarded as a kind of extended ETAr derivatives (Chart 1), in which the auxiliary ethynylthieno[3,2-*b*]thiophene spacer is inserted between the benzene rings.

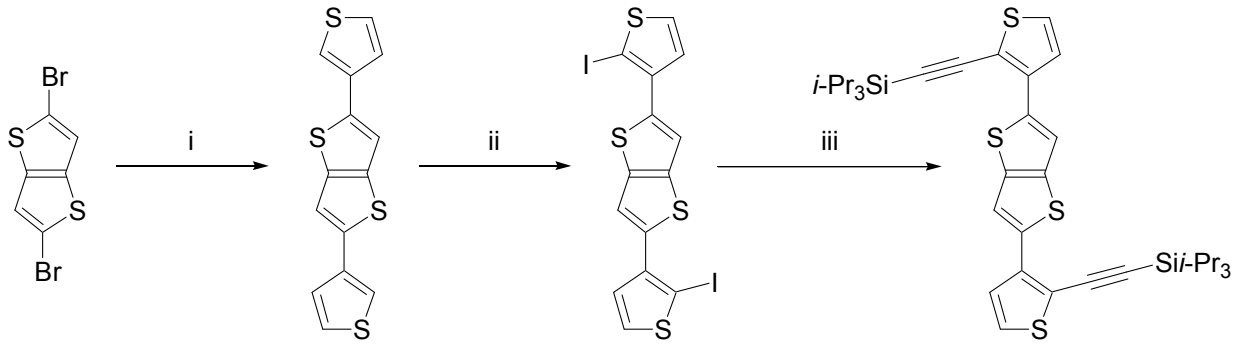


Reagents and conditions: i, ethynyltriisopropylsilane, CuI, $PdCl_2(PPh_3)_2$, *i*-Pr_2NH, THF;
ii, **8a**, $Pd(PPh_3)_4$, K_2CO_3, THF, toluene, H_2O; iii, **12**, $Pd(PPh_3)_4$, K_2CO_3, THF, toluene, H_2O.

Scheme 2

A related compound **20**, containing thienothiophene moiety between the thiophene rings, was also prepared (Scheme 3): Suzuki-Miyaura cross coupling reaction of 3-thiopheneboronic acid with 2,5-dibromothieno[3,2-*b*]thiophene (**17**)[21] afforded **18**. Compound **18** was almost insoluble in common solvent, however, a suspension of **18** and *N*-iodosuccinimide (NIS) in AcOH-$CHCl_3$ under thermal conditions gave diiodo derivative **19** as a crude product. It should be mentioned that reaction of **18** with 1 equiv. (2 molar amounts) of NIS may lead to an over-iodinated product and recovery of unreacted **18**, because **19** is more soluble (in AcOH-$CHCl_3$) than **18**. In order to avoid the over reaction, 0.5 equiv. (1 molar amount) of NIS was used in the reaction described above (85% yield based on NIS used).

Sonogashira reaction of **19** with ethynyltriisopropylsilane afforded the desired **20** in 37% yield after purification.



17 **18** **19** **20**

Reagents and conditions: i, 3-thiopheneboronic acid, $Pd(PPh_3)_4$, K_2CO_3, 1,4-dioxane, H_2O; ii, *N*-iodosuccinimide, AcOH, $CHCl_3$, AIBN, iii, ethynyltriisopropylsilane, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF.

Scheme 3

Figure 1 shows UV-visible spectra of the ETB derivative **1a**,[6] ethynylthienothiophene derivative **7a**, symmetrically substituted derivative **9**, and 1-(thieno[3,2-*b*]thiophen-2-yl)-4-(3-thienyl)benzene derivatives **15** and **16** in CH_2Cl_2. When the thiophene ring of **1a** is replaced to thienothiophene ring, the spectra shifted to the longer wavelength: A bathochromic shift is observed in the order **1a**<**15**<**9**. When the [(triisopropylsilylethynyl)thienyl]phenyl groups are substituted to the ethynylthienothiophene **7a**, large bathochromic shift is observed in the order **7a**<**15**<**16**, indicating efficient π conjugation of the [(triisopropylsilylethynyl)thienyl]phenyl moiety with the central thienothiophene moiety.

Figure 2 exhibits UV-visible spectra of the triisopropylsilyl derivatives **1a** and **9**, hexylphenyl derivative **1b**[7] (data taken from ref. 22), unsymmetrically substituted derivative **11**, and 2,5-dithienyl-thieno[3,2-*b*]thiophene derivative **20** in CH_2Cl_2. As expected from the difference between the spectra of **1a** and **1b**, compound **11** showed a red shift, compared to **9**. Central thienothiophene moiety causes large bathochromic shift, compared to the central benzene ring: This is shown by comparison of the spectra of compounds **1a** and **20**. It should be mentioned that the large red shift of **20** is in contrast with the case of ETAr spacer (Chart 1) containing a biphenyl moiety. Effect of central biphenyl moiety in the ETAr spacer has turned out to be not so large: A spectrum of 4,4'-bis[2-(trimethylsilyl-ethynyl)-3-thienyl)]biphenyl [λ_{max}/nm 271 (log ε 4.51), 293 (4.52), 302 (4.52), 329 (4.56)][7] is similar to that of **1c** [λ_{max}/nm 259 (log ε 4.46), 289 (4.45), 327 (4.38)],[6] from viewpoint of λ_{max} value of the absorption band with the longest wavelength. The absorption band with the longest wavelength. The different electronic and structural character of the central moieties (i.e., thienothiophene moiety) may work in the tuning of the ETB/ETAr system.

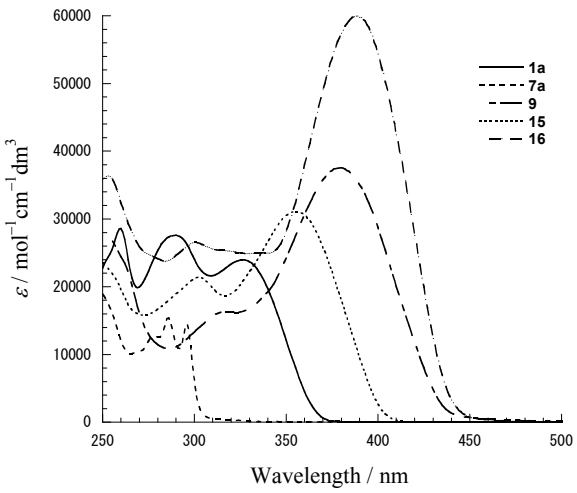


Figure 1. UV-vis spectra of **1a**, **7a**, **9**, **15**, and **16**.

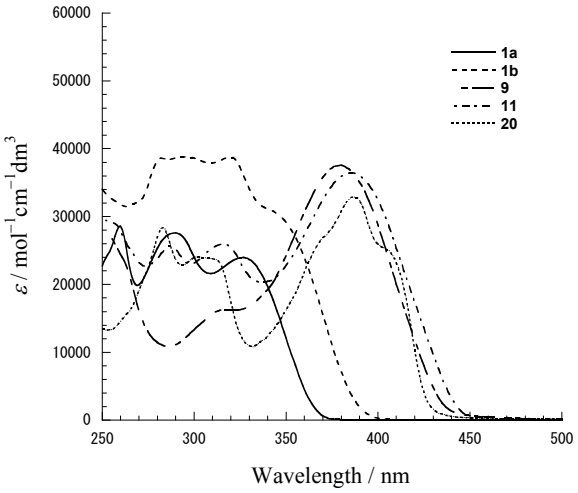


Figure 2. UV-vis spectra of **1a**, **1b**,[22] **9**, **11**, and **20**.

In summary, we have prepared various compounds containing thieno[3,2-*b*]thiophene moieties. They have trialkylsilylethynyl branches on the 3-position of the thienothiophene moieties and/or 2-position of the thiophene moieties. Some of them have pseudoaxes through the 2- and 5-positions of the thienothiophene moieties. Extension of π-system through the central benzene ring (or thienothiophene ring) was suggested by UV-vis spectra. These ETB-related units will help construction of larger systems, by linking the units, like the case of compound **3**.

EXPERIMENTAL

Melting points were measured on a Yanagimoto MP-J3 micro melting points apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance-400 or a JEOL ECA-600 spectrometer. UV-vis spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Shimadzu FTIR-8100M spectrometer. MS spectra were taken on a Hitachi M-2500S spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer.

3-[2-(Triisopropylsilyl)ethynyl]thieno[3,2-*b*]thiophene (7a). A mixture of 3-bromothieno-[3,2-*b*]thiophene (**6**) (1.27 g, 5.80 mmol), ethynyltriisopropylsilane (1.93 mL, 8.69 mmol), dichlorobis(triphenylphosphine)palladium(II) (94.4 mg, 0.134 mmol), copper(I) iodide (25.8 mg, 0.136 mmol), and diisopropylamine (10 mL) in 1,4-dioxane (50 mL) was refluxed under nitrogen atmosphere for 43 h. After cooling to room temperature, $CHCl_3$ and water were added to the filtrate. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane) to give 1.80 g (5.62 mmol, 97% yield) of **7a**: Colorless oil; R_f = 0.33 (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.15 (21H, s, *i*-Pr),

7.28 (1H, d, ^3J = 5.2 Hz), 7.41 (1H, dd, ^3J = 5.2 Hz and ^5J = 1.6 Hz), and 7.51 (1H, d, ^5J = 1.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 11.2 (*C*HMe_2), 18.7 (Me), 93.6 (C≡C), 99.6 (C≡C), 115.6, 119.7, 128.0, 130.6, 138.0 and 141.7; UV (CH_2Cl_2) 248 (log ε 4.28), 278 (4.10), 286 (4.19), and 296 nm (4.16); IR (neat) 3104, 2944, 2892, 2865, 2145 (C≡C), 1495, 1461, 1383, 1366, 1347, 1244, 1192, 1167, 1092, 1076, 1017, 995, 909, 884, 847, 797, 752, 716, 677, 650, 559, 505, 471, and 455 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 320 (M^+; 58), 277 (M^+–*i*-Pr; 100), 249 (M^+–*i*-Pr–2Me+2; 26), 235 (M^+–2*i*-Pr+1; 35), 221 (M^+–2*i*-Pr–Me+2; 27), and 207 (M^+–*i*-Pr_2Si+1; 41). Calcd for $C_{17}H_{24}S_2Si$: M, 320.1089. Found: *m*/*z* 320.1084.

3-[2-(4-Hexylphenyl)ethynyl]thieno[3,2-*b*]thiophene (7b). A mixture of **6** (142.0 mg, 0.648 mmol), 1-ethynyl-4-hexylbenzene (199.9 mg, 1.073 mmol), dichlorobis(triphenylphosphine)palladium(II) (22.0 mg, 0.0313 mmol), copper(I) iodide (3.1 mg, 0.016 mmol), and diisopropylamine (2 mL) in 1,4-dioxane (10 mL) was stirred at 80 °C for 2 d. After cooling to room temperature, $CHCl_3$ (ca. 100 mL) and water (ca. 100 mL) were added. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane) to give 182.0 mg (0.5608 mmol, 87% yield) of **7b**: Colorless oil; R_f = 0.30 (SiO_2-hexane); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.88 (3H, t, ^3J = 6.8 Hz, Me), 1.2–1.3 (6H, m, CH_2), 1.61 (2H, quin, ^3J = 7.6 Hz, CH_2), 2.61 (2H, t, ^3J = 7.6 Hz, CH_2), 7.17 (2H, ^3J = 8.1 Hz, phenyl), 7.24 (1H, d, ^3J = 5.2 Hz), 7.43 (1H, dd, ^3J = 5.2 Hz and ^5J = 1.5 Hz), 7.47 (2H, d, ^3J = 8.1 Hz, phenyl), and 7.54 (1H, d, ^5J = 1.5 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 14.1 (Me), 22.6 (CH_2), 28.9 (CH_2), 31.2 (CH_2), 31.6 (CH_2), 35.9 (CH_2), 81.9 (C≡C), 91.8 (C≡C), 115.3, 119.7, 119.9, 127.9, 128.5, 130.0, 131.5, 138.2, 141.0, and 143.7; UV (CH_2Cl_2) 262 (sh, log ε 4.37), 270 (4.46), 287 (sh, 4.34), 296 (4.42), 304 (4.39), and 315 nm (4.37); IR (neat) 3102, 2955, 2928, 2855, 2217 (C≡C, weak), 1520, 1466, 1350, 1088, 1051, 1019, 909, 853, 835, 818, 797, 714, 650, 563, and 529 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 324 (M^+; 83), and 253 (M^+–C_5H_{11}; 100). Calcd for $C_{20}H_{20}S_2$: M, 324.1006. Found: *m*/*z* 323.9369.

3-[2-(Trimethylsilyl)ethynyl]thieno[3,2-*b*]thiophene (7c). A mixture of **6** (184.5 mg, 0.843 mmol), ethynyltrimethylsilane (99.5 mg, 1.01 mmol), dichlorobis(triphenylphosphine)palladium(II) (32.8 mg, 0.0468 mmol), copper(I) iodide (10.3 mg, 0.0541 mmol), and diisopropylamine (2 mL) in THF (10 mL) was stirred under nitrogen atmosphere at 70 °C for 28 h. After cooling to room temperature, $CHCl_3$ (ca. 100 mL) and water (ca. 100 mL) were added to the filtrate. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography ($CHCl_3$) to give a mixture of 3-[2-(trimethylsilyl)ethynyl]thieno-[3,2-*b*]thiophene and the starting **6**. To this mixture, were added ethynyltrimethylsilane (54.5 mg, 0.555 mmol), dichlorobis(triphenylphosphine)palladium(II) (11.9 mg, 0.017 mmol), copper(I) iodide (5.7 mg, 0.030 mmol), diisopropylamine (1 mL), and 1,4-dioxane (5 mL). The resulting mixture was stirred

under nitrogen atmosphere at 101 °C for 20 h. After cooling to room temperature, $CHCl_3$ and water were added to the filtrate. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane) to give 179.2 mg (0.758 mmol, 90% yield) of **7c**: Colorless oil; R_f = 0.26 (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (9H, s, Me), 7.23 (1H, d, ^3J = 5.2 Hz), 7.42 (1H, dd, ^3J = 5.2 Hz and ^5J = 1.6 Hz), and 7.53 (1H, d, ^5J = 1.6 Hz); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = –0.5 (Me), 97.1 (C≡C), 97.8 (C≡C), 115.2, 119.7, 128.1, 131.3, 138.1, and 141.2; IR (neat) 3104, 2959, 2899, 2161, 2147 (C≡C), 2068, 1491, 1468, 1347, 1250, 1192, 1167, 1090, 1078, 909, 858, 843, 797, 760, 714, 650, 558, and 471 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 236 (M^+; 63) and 221 (M^+–Me; 100). Calcd for $C_{11}H_{12}S_2Si$: M, 236.0150. Found: *m/z* 236.0145.

1,4-Bis[3-{2-(triisopropylsilyl)ethynyl}thieno[3,2-*b*]thiophen-2-yl]benzene (9). To a solution of **7a** (90.6 mg, 0.283 mmol) in THF (5 mL) was added 0.43 mmol of butyllithium (1.65 M solution in hexane, 0.26 mL) at –78 °C and the resulting mixture was stirred for 40 mim. To the solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.090 mL, 0.441 mmol) at 0 °C, and the reaction mixture was stirred for 45 min. To the resulting mixture were added water (ca. 100 mL) and EtOAc (ca. 100 mL), the organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude **8a**. This crude product was used in the following reaction without further purification. **8a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.18 (21H, s, *i*-Pr), 1.25 (12H, s, CMe_2), 7.22 (1H, d, ^3J = 5.2 Hz), and 7.47 (1H, d, ^3J = 5.2 Hz). A mixture of crude **8a** (ca. 0.27 mmol), 1,4-diiodobenzene (43.9 mg, 0.133 mmol), tetrakis(triphenylphosphine)palladium (14.5 mg, 0.0125 mmol), K_2CO_3 (180.3 mg), THF (2.5 mL), toluene (2.5 mL), and water (1 mL) was heated at 85 °C for 20 h. After cooling to rt, $CHCl_3$ (ca. 100 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane-EtOAc: 10:1 to 0:1) to give 12.8 mg of **9** (0.0179 mmol, 13% yield based on the starting **7a**). **9**: Pale yellow solid, mp 162–165 °C; R_f = 0.16 (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.17 (42H, s, *i*-Pr), 7.23 (2H, d, ^3J = 5.2 Hz), 7.41 (2H, d, ^3J = 5.2 Hz), and 8.04 (4H, s, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 11.2 (*C*HMe_2), 18.7 (Me), 98.0 (C≡C), 100.4 (C≡C), 111.3, 119.7, 127.5, 134.0, 135.5, 143.8, and 146.9; UV-vis (CH_2Cl_2) 250 (log ε 4.45), 320 (4.21), and 380 nm (4.57); IR (KBr) 2940, 2863, 2141, 1524, 1462, 1356, 994, 943, 912, 882, 833, 808, 708, 663, and 640 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 714 (M^+; 100), 157 (*i*-Pr_3Si^+; 18), and 115 (*i*-Pr_2Si^++1; 13). Calcd for $C_{40}H_{50}S_4Si_2$: M, 714.2334. Found: *m/z* 714.2331.

1-Bromo-4-[3-{2-(triisopropylsilyl)ethynyl}thieno[3,2-*b*]thiophen-2-yl]benzene (10). A mixture of 1-bromo-4-iodobenzene (783.7 mg, 2.77 mmol), crude **8a** [prepared from 517.2 mg (1.613 mmol) of **7a**

by the method described above], tetrakis(triphenylphosphine)palladium (44.8 mg, 0.0388 mmol), K_2CO_3 (1.12 g), THF (15 mL), toluene (15 mL), and water (8 mL) was heated at 70 °C for 13 h. After cooling to room temperature, $CHCl_3$ (ca. 200 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure. To the residue was added hexane and an insoluble material was removed by filtration. The filtrate was concentrated under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane-$CHCl_3$, 1:0 to 0:1) to give 160.6 mg (0.3377 mmol, 21% yield based on the starting **7a**) of **10**: Pale yellow solid, mp 70–72 °C; R_f = 0.35 (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.16 (21H, s, *i*-Pr), 7.22 (1H, d, ^3J = 5.2 Hz), 7.41 (1H, d, ^3J = 5.2 Hz), 7.52 (2H, d, ^3J = 8.4 Hz, phenyl), and 7.88 (2H, d, ^3J = 8.4 Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 11.3 (*C*HMe$_2$), 18.7 (Me), 98.1 (C≡C), 100.1 (C≡C), 111.4, 119.6, 122.2, 127.6, 128.8, 131.6, 133.1, 135.4, 143.6, and 146.0; IR (KBr) 2957, 2888, 2861, 2149 (C≡C), 1505, 1483, 1464, 1397, 1356, 1190, 1059, 955, 912, 884, 820, 777, 712, 561, 504, and 426 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 476 (M^++2; 100), 474 (M^+; 85), 433 (M^+–*i*-Pr+2; 76), 431 (M^+–*i*-Pr; 68), 363 (M^+–*i*-Pr$_2$Si+3; 35), 361 (M^+–*i*-Pr$_2$+1; 34), 309 (M^+–Br–*i*-Pr$_2$; 59), and 188 (M^+–Br–*i*-Pr$_3$SiC$_2$–S–1; 36); Found: *m/z* 474.0505. Calcd for $C_{23}H_{27}BrS_2Si$: M, 474.0507. Anal. Calcd for $C_{23}H_{27}S_2Si$: C, 58.09; H, 5.72%. Found: C, 58.47; H, 5.85%.

1-[3-{2-(4-Hexylphenyl)ethynyl}thieno[3,2-*b*]thiophen-2-yl]-4-[3-{2-(triisopropylsilyl)ethynyl}-thieno[3,2-*b*]thiophen-2-yl]benzene (11). To a solution of **7b** (82.8 mg, 0.255 mmol) in THF (4.5 mL) was added 0.25 mmol of butyllithium (1.65 M solution in hexane, 0.15 mL) at –78 °C and the resulting mixture was allowed to warm to 0 °C and stirred for 20 min. To the solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.05 mL, 0.25 mmol) and the reaction mixture was allowed to warm to room temperature. To the resulting mixture were added water (ca. 100 mL) and EtOAc (ca. 100 mL), the organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude **8b**. **8b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (3H, t, ^3J = 6.8 Hz, Me), 1.32 (6H, m, CH_2), 1.40 (12H, s, CMe_2), 1.61–1.64 (2H, m, CH_2), 2.63 (2H, t, ^3J = 7.8 Hz, CH_2), 7.18 (2H, d, ^3J = 8.0 Hz, phenyl), 7.25 (1H, d, ^3J = 5.2 Hz), 7.51 (1H, d, ^3J = 5.2 Hz), and 7.52 (2H, d, ^3J = 8.0 Hz, phenyl). A mixture of the crude **8b**, **10** (106.4 mg, 0.224 mmol), tetrakis(triphenylphosphine)palladium (6.9 mg, 0.0060 mmol), K_2CO_3 (177 mg), THF (5 mL), toluene (5 mL), and water (2 mL) was heated at 85 °C for 17 h. After cooling to room temperature, $CHCl_3$ (ca. 100 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane-$CHCl_3$, 1:0 to 0:1) to give 99.4 mg (0.138 mmol, 62% yield based on **10**) of **11**. **11**: Yellow oil; R_f = 0.14 (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (3H, t, ^3J = 6.8 Hz, Me), 1.15 (21H, s, *i*-Pr), 1.31 (6H, m, CH_2), 1.62 (2H, m, CH_2),

2.63 (2H, t, ^3J = 7.6 Hz, CH_2), 7.19 (2H, d, ^3J = 8.4 Hz, phenyl), 7.24 (1H, d, ^3J = 5.2 Hz), 7.26 (1H, d, ^3J = 5.2 Hz), 7.41 (1H, d, ^3J = 5.2 Hz), 7.43 (1H, d, ^3J = 5.2 Hz), 7.49 (2H, d, ^3J = 8.4 Hz, phenyl), 8.04 (2H, d, ^3J = 8.4 Hz, phenyl), and 8.13 (2H, d, ^3J = 8.4 Hz, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 11.3 (*C*HMe_2), 14.1 (CH_2*Me*), 18.7 (CH*Me*$_2$), 22.6 (CH_2), 28.9 (CH_2), 31.2 (CH_2), 31.7 (CH_2), 35.9 (CH_2), 82.8 (C≡C), 95.3 (C≡C), 98.2 (C≡C), 100.5 (C≡C), 111.1, 111.2, 119.7, 120.0, 127.3, 127.4, 127.5, 128.5, 131.6, 133.9, 134.2, 135.4, 135.6, 143.0, 143.8, 143.8, 146.1, and 146.9; UV-vis (CH_2Cl_2) 248 (log ε 4.48), 253 (sh, 4.47), 287 (4.41), 316 (4.41), and 386 nm (4.56); IR (KBr) 2926, 2862, 2147 (C≡C), 1516, 1464, 1358, 1339, 1067, 995, 943, 910, 833, 710, 665, 635, and 529 cm^{-1}. Calcd for $C_{43}H_{46}NaS_4Si$: $(M+Na)^+$, 741.2144. Found: *m/z* 741.2143.

1-Bromo-4-[2-{2-(triisopropylsilyl)ethynyl}-3-thienyl]benzene (14). 1-Bromo-4-(2-iodo-3-thienyl)-benzene (**13**) was prepared according to the previously reported method [9] [^1H NMR ($CDCl_3$) δ = 6.94 (1H, d), 7.38 (2H, AA'BB'), 7.50 (1H, d), and 7.57 (2H, AA'BB')]. A mixture of **13** (1.047 g, 2.87 mmol), ethynyltriisopropylsilane (0.65 mL, 2.9 mmol), dichlorobis(triphenylphosphine)palladium(II) (105.2 mg, 0.15 mmol), copper(I) iodide (41 mg, 0.22 mmol), and diisopropylamine (40 mL) in THF (40 mL) was stirred at 50 °C for 116 h. After cooling to room temperature, $CHCl_3$ (ca. 200 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane) to give 1.035 g (2.47 mmol, 86% yield) of **14**: Colorless oil; R_f = 0.47 (SiO_2-hexane); ^1H NMR (400 MHz, $CDCl_3$) δ = 1.10 (21H, br s, *i*-Pr), 7.15 (1H, d, ^3J = 5.5 Hz, thienyl), 7.24 (1H, d, ^3J = 5.5 Hz, thienyl), 7.50 (2H, d, ^3J = 8.5 Hz, phenyl), and 7.72 (2H, d, ^3J = 8.5 Hz, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 11.3 (*C*HMe_2), 18.6 (Me), 99.0 (C≡C), 99.3 (C≡C), 118.9 (2-thienyl), 121.5 (1-Ph), 126.4 (4-thienyl), 127.2 (5-thienyl), 129.5 (3- and 5-Ph), 131.4 (2- and 6-Ph), 134.0 (4-Ph), and 143.4 (3-thienyl); IR (neat) 2938, 2865, 2141 (C≡C), 1592, 1524, 1487, 1464, 1368, 1277, 1067, 1011, 997, 888, 824, 762, 733, 677, and 663 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 420 (M^++2; 48), 418 (M^+; 45), 377 (M^+–*i*-Pr+2; 100), 375 (M^+–*i*-Pr; 95), 307 (M^+–2*i*-Pr–Si+3; 30), 305 (M^+–2*i*-Pr–Si+1; 27), and 253 (M^+–2*i*-Pr–Br; 35). Calcd for $C_{21}H_{27}BrSSi$: M, 418.0786. Found: *m/z* 418.0787.

1-[3-{2-(Triisopropylsilyl)ethynyl}thieno[3,2-*b*]thiophen-2-yl]-4-[2-{2-(triisopropylsilyl)ethynyl}-3-thienyl]benzene (15). A mixture of **14** (732.0 mg, 1.75 mmol), crude **8a** [prepared from 500.7 mg (1.56 mmol) of **7a** by the method described above], tetrakis(triphenylphosphine)palladium (38.8 mg, 0.0336 mmol), K_2CO_3 (1.08 g), THF (15 mL), toluene (15 mL), and water (8 mL) was heated at 85 °C for 17 h. After cooling to room temperature, $CHCl_3$ (ca. 200 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography

(hexane-$CHCl_3$, 1:0 to 0:1) to give 363.9 mg of crude **15** and 227.7 mg of crude **16**. The crude **15** was recrystallized from hexane to give 213.0 mg (0.323 mmol, 21% yield based on the starting **7a**) of **15**. The crude **16** was recrystallized from $CHCl_3$ to give 122.7 mg (0.123 mmol, 8% yield based on the starting **7a**) of **16**. **15**: Pale yellow solid, mp 130–134 °C (decomp); R_f = 0.22 (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.11 (21H, s, *i*-Pr), 1.17 (21H, s, *i*-Pr), 7.22 (1H, d, ^3J = 5.2 Hz), 7.23 (1H, d, ^3J = 5.2 Hz), 7.26 (1H, d, ^3J = 5.2 Hz), 7.40 (1H, d, ^3J = 5.2 Hz), 7.87 (2H, d, ^3J = 8.4 Hz, phenyl), and 8.03 (2H, d, ^3J = 8.4 Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 11.3 (*C*HMe$_2$), 18.7 (Me), 97.7 (C≡C), 98.9 (C≡C), 99.6 (C≡C), 100.5 (C≡C), 111.1, 118.8, 119.7, 126.3, 127.2, 127.3, 127.6, 128.1, 133.3, 135.1, 135.3, 143.8, 144.1, and 147.4; UV-vis (CH_2Cl_2) 248 (log ε 4.38), 303 (4.33), and 356 nm (4.49); IR (KBr) 2942, 2865, 2137 (C≡C), 1534, 1462, 1381, 1356, 1094, 1017, 995, 957, 882, 839, 776, 762, 743, 712, 677, 623, 538, 507, and 467 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 658 (M^+; 100), 157 (*i*-Pr_3Si^+; 43), and 115 (*i*-Pr_2Si^++1; 20); Found: *m*/*z* 658.2614. Calcd for $C_{38}H_{50}S_3Si_2$: M, 658.2613. Anal. Calcd for $C_{38}H_{50}S_3Si_2$: C, 69.24; H, 7.65%. Found: C, 69.41; H, 7.72%.

Preparation of compound 16. To a solution of **7a** (45.1 mg, 0.141 mmol) in THF (3 mL) was added 0.30 mmol of butyllithium (1.65 M solution in hexane, 0.18 mL) at –78 °C, the resulting mixture was allowed to warm to 0 °C, and stirred for 30 min. To the solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.070 mL, 0.34 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. To the resulting mixture were added water (ca. 100 mL) and EtOAc (ca. 100 mL), the organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude **12**. **12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.17–1.18 (21H, br s, *i*-Pr), 1.34 (12H, s, OCMe$_2$), 1.36 (12H, s, OCMe$_2$), and 7.71 (1H, s, thienothiophene). A mixture of **14** (122.1 mg, 0.2911 mmol), the crude **12**, tetrakis(triphenylphosphine)palladium (7.4 mg, 0.0064 mmol), K_2CO_3 (256 mg), THF (5 mL), toluene (5 mL), and water (3 mL) was heated at 85 °C for 16 h. After cooling to room temperature, $CHCl_3$ (ca. 100 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica-gel column chromatography (hexane - $CHCl_3$, 1:0 to 5:1) to give 81.4 mg (0.0816 mmol, 58% yield based on **7a**) of **16**: Yellow solid, mp 184–189 °C (decomp); R_f = 0.05 (SiO_2-hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.12-1.16 (42H, *i*-Pr), 1.20-1.22 (21H, *i*-Pr), 7.19 (1H, d, ^3J = 5.3 Hz), 7.20 (1H, d, ^3J = 5.3 Hz), 7.24 (1H, d, ^3J = 5.3 Hz), 7.24 (1H, d, ^3J = 5.3 Hz), 7.43 (1H, s), 7.64 (2H, d, ^3J = 8.6 Hz, phenyl), 7.87 (2H, d, ^3J = 8.8 Hz, phenyl), 7.89 (2H, d, ^3J = 8.6 Hz, phenyl), and 8.04 (2H, d, ^3J = 8.8 Hz, phenyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 11.4 (C*H*Me$_2$ x 3), 18.7 (Me x 3), 97.9 (C≡C), 98.9 (C≡C), 98.9 (C≡C), 99.6 (C≡C), 99.7 (C≡C), 100.4 (C≡C), 111.2, 115.5, 118.7, 118.8, 125.7, 126.3, 126.4, 127.2, 127.4, 127.6, 128.1, 128.5, 133.2, 133.6, 134.8, 135.1, 136.2, 143.1, 144.1, 144.1, 146.1, and 146.8;

UV-vis (CH_2Cl_2) 253 (log ε 4.56), 274 (sh, 4.40), 301 (4.42), and 389 nm (4.78); IR (KBr) 2942, 2890, 2865, 2136 (C≡C), 1534, 1505, 1462, 1383, 1366, 1092, 1075, 1061, 1017, 995, 882, 841, 814, 762, 743, 712, 677, 57, and 465 cm^{-1}; Found: *m/z* 1019.4029. Calcd for $C_{59}H_{76}NaS_4Si_3$: $(M+Na)^+$, 1019.4030. Anal. Calcd for $C_{59}H_{76}S_4Si_3 \cdot H_2O$: C, 69.76; H, 7.74%. Found: C, 70.16; H, 7.68%.

2,5-Di(3-thienyl)thieno[3,2-*b*]thiophene (18). A mixture of 2,5-dibromothieno[3,2-*b*]thiophene (**17**) (510.2 mg, 1.71 mmol), 3-thiopheneboronic acid (472g, 3.69 mmol), tetrakis(triphenylphosphine)-palladium (22.6 mg, 0.020 mmol), K_2CO_3 (1.15 g), 1,4-dioxane (50 mL), and water (30 mL) was heated under nitrogen at 100 °C for 1.5 h. Insoluble material was collected by filtration and washed with $CHCl_3$ (ca. 50 mL) to give **18** (462.7 mg, 1.52 mmol) in 89% yield. This compound was almost insoluble in common solvents and used in the succeeding reaction without recrystallization. **18**: Pale yellow solid, mp > 300 °C; IR (KBr) 3096, 3083, 1638, 1543, 1470, 1404, 1375, 1327, 1248, 1213, 1194, 1179, 1088, 1013, 1005, 947, 911, 872, 855, 841, 818, 681, 662, 633, 536, and 453 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 304 (M^+; 100), 259 (M^+–S–CH; 6), and 152 (M^+/2; 7). Calcd for $C_{14}H_8S_4$: M^+, 303.9509. Found: *m/z* 303.9505.

2,5-Bis(2-iodo3-thienyl)thieno[3,2-*b*]thiophene (19). A suspension of **18** (119.8 mg, 0.393 mmol), *N*-iodosuccinimide (NIS, 88.9 mg, 0.395 mmol, 1.01 molar ratio based on **18**), and acetic acid (5 mL) in $CHCl_3$ (10 mL) was stirred at 60 °C for 3 h. The insoluble starting material **18** (25.3 mg) was recovered by filtration in 21% recovery. $CHCl_3$ (ca. 20 mL) and water (ca. 20 mL) were added to the filtrate and the organic phase was separated, washed with saturated aqueous $NaHCO_3$ solution, and then washed with saturated aqueous $NaHSO_3$ solution. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with a silica-gel column chromatography (CCl_4) to give 93.0 mg (0.167 mmol, 85% yield based on NIS) of **19**: Yellow solid, mp 176–178 °C; R_f = 0.55 (SiO_2-CCl_4); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.07 (2H, d, ^3J = 5.5 Hz, 4-thienyl), 7.50 (2H, d, ^3J = 5.5 Hz, 5-thienyl), and 7.61 (2H, s); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 73.0 (2-thienyl), 118.5, 128.9 (4-thienyl), 131.6 (5-thienyl), 139.0, and 139.7 (thienothiophene and 3-thienyl); IR (KBr) 3094, 1487, 1387, 1320, 1240, 1053, 955, 905, 837, 826, 723, 716, 669, 627, and 544 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 556 (M^+; 100), 430 (M^+–I+1; 10), and 302 (M^+–2I; 18). Calcd for $C_{14}H_6I_2S_4$: M, 555.7442. Found: *m/z* 555.7443.

2,5-Bis[2-{2-(triisopropylsilyl)ethynyl}-3-thienyl]thieno[3,2-*b*]thiophene (20). A mixture of **19** (72.8 mg, 0.131 mmol), ethynyltriisopropylsilane (0.123 mL, 0.672 mmol), dichlorobis(triphenylphosphine)-palladium(II) (21.7 mg, 0.031 mmol), copper(I) iodide (6.7 mg, 0.035 mmol), and diisopropylamine (10 mL) in THF (15 mL) was stirred under nitrogen atmosphere at 60 °C for 40 h. $CHCl_3$ (ca. 20 mL) and water (ca. 20 mL) were added to the reaction mixture. The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure, the residue was treated with a silica-gel

column chromatography (CCl_4) to give a crude product (77.7 mg, ca. 90% yield), which was purified by additional silica-gel column (CCl_4) to give 32.2 mg (0.048 mmol, 37% yield) of **20**: Yellow solid, mp 148–149 °C; R_f = 0.60 (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.18 (s, 42H, s, *i*-Pr), 7.21 (s, 4H, 4- and 5-thienyl), and 7.94, (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 11.3 (*C*HMe$_2$), 18.6 (Me), 99.5 (C≡C), 101.6 (C≡C), 117.0, 117.6, 126.3, 126.6, 137.9, 138.9, and 139.7; UV-vis (CH_2Cl_2) 283 (log ε 4.45), 308 (4.38), 370 (sh, 4.43), 387 (4.52), and 406 (sh, 4.40); IR (KBr) 2942, 2865, 2137 (C≡C), 1462, 1092, 1051, 1017, 994, 882, 847, 826, 812, 758, 727, 644, 613, and 534 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 664 (M^+; 100), 579 (M^+–2*i*-Pr+1; 8), and 537 (M^+–3*i*-Pr+2; 4); Found: *m/z* 664.2175. Calcd for $C_{36}H_{48}S_4Si_2$: M, 664.2177. Anal. Calcd for $C_{36}H_{48}S_4Si_2$: C, 65.00; H, 7.27%. Found: C, 65.02; H, 7.26%.

ACKNOWLEDGEMENTS

This work was supported in part by the Grants-in-Aid for Scientific Research (No. 20550030) from the Ministry of Education, Culture, Sports, Science and Technology.

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