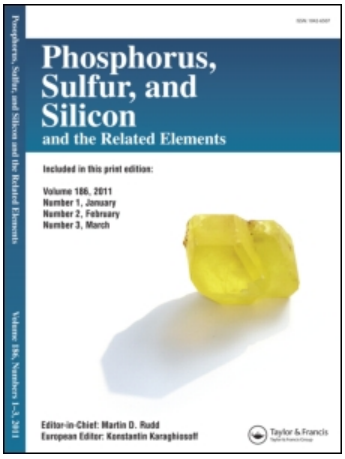

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Chemistry of Bis(2-ethynyl-3-thienyl)arene and Related Systems, Part 5: Preparation of an Unsymmetrical 4,4'-Bis(3-thienyl)biphenyl Derivative Containing a 2-[2-(Diphenylphosphino)ethynyl]-3-thienyl Moiety

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CHEMISTRY OF BIS(2-ETHYNYL-3-THIENYL)ARENE AND RELATED SYSTEMS, PART 5: PREPARATION OF AN UNSYMMETRICAL 4,4′-BIS(3-THIENYL)BIPHENYL DERIVATIVE CONTAINING A 2-[2-(DIPHENYLPHOSPHINO)ETHYNYL]-3-THIENYL MOIETY

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An unsymmetrically substituted 4,4′-bis(3-thienyl)biphenyl derivative of 4-(2-ethynyl-3-thienyl)-4′-(3-thienyl)biphenyl type was prepared, utilizing 4-bromo-4′-(2-iodo-3-thienyl) biphenyl as synthetic intermediate. Reaction of 4-(2-ethynyl-3-thienyl)-4′-(3-thienyl) biphenyl with ethylmagnesium bromide followed by treatment with chlorodiphenylphosphine afforded 4-[2-(2-diphenylphosphinoethynyl)-3-thienyl]-4′-(3-thienyl)biphenyl.

Keywords Artificial enzyme; artificial molecular architecture; heterocycles; oligoarene; phosphorus ligand

INTRODUCTION

Artificial enzymes[1] as well as artificial molecular architecture[2] are of current interest. In the course of our continuing research on developing novel phosphorus ligands, such as DPCBT[3,4] and related polymers[5] (Figure 1) as well as transition metal catalysts,[6,7] we designed 1,4-bis(2-ethynyl-3-thienyl)arene spacers [hereafter abbreviated as ETAr (Figure 1, $n \geq 2$) or ETB ($n = 1$) spacers]. We have already prepared several compounds such as **1a**,**b**–**3a**,**b** containing the ETB or ETAr spacer[8–11] (Figure 2). In addition, we recently prepared the unsymmetrical ETB derivative **6** as well as monoethynyl compounds **4**, **5**, and linked ETB compound **7**.[9,10] These compounds are promising building blocks for the linked ETB system[9] (Figure 1). For construction of more sophisticated systems such as artificial enzymes, development of unsymmetrical 4,4′-bis(3-thienyl)biphenyl building

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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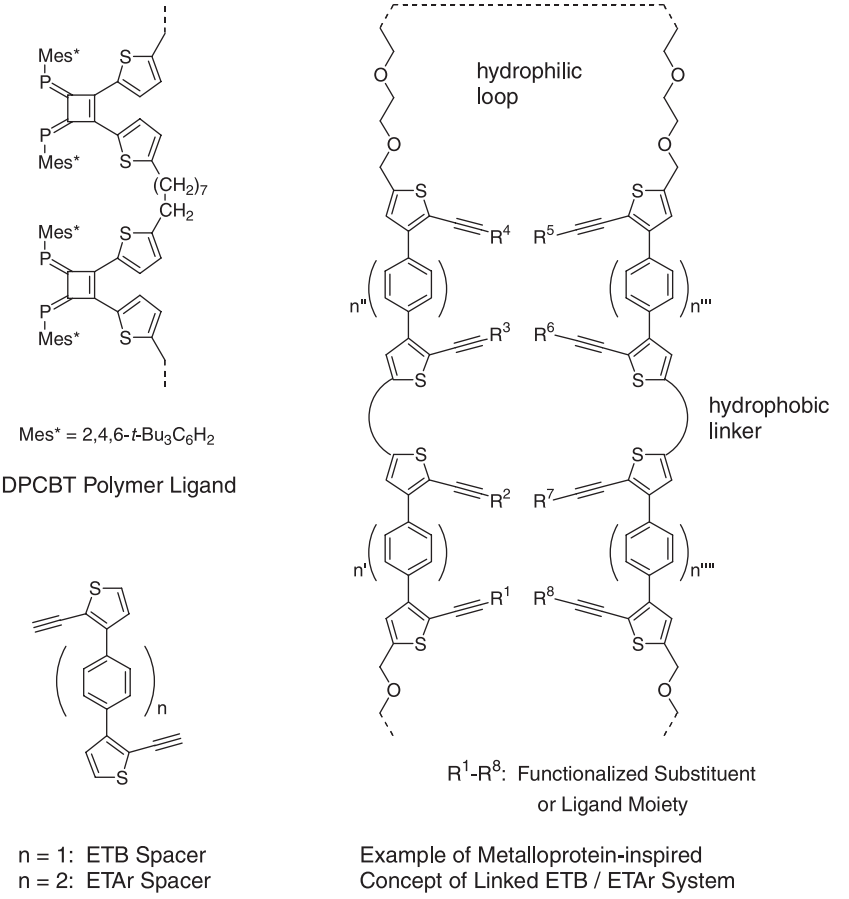


Figure 1 Some spacers and systems containing thiophene.

blocks is desirable. We report in this article the preparation of unsymmetrical 4,4′-bis(3-thienyl)biphenyl derivative **8** containing phosphorus ligand moiety, which may be regarded as a part of a catalytic center of the ETB/ETAr-linked catalyst system.

RESULTS AND DISCUSSION

In our previously reported synthetic route to unsymmetrical 1,4-bis(2-ethynyl-3-thienyl)benzene derivatives,[10] 1-bromo-4-(2-iodo-3-thienyl)benzene was used as a key synthetic intermediate, because an ethynyl group can be introduced predominantly in the 2-position of the thiophene ring by the Sonogashira coupling reaction, and not in the benzene ring or other positions, due to different reactivity of the iodo- and bromo-substituent. Thus, in the present report, utilization of a similar intermediate, 4-bromo-4′-(2-iodo-3-thienyl)biphenyl (**11**), was planned for the preparation of **8** (Scheme 1). 4-Bromo-4′-(3-thienyl)biphenyl (**10**) was prepared from either 4,4′-dibromobiphenyl (Scheme 1, Route A) or 1-iodo-4-(3-thienyl)benzene (**9**) (Route B). In the reaction of 4,4′-dibromobiphenyl with 3-thiopheneboronic acid (Route A), compounds **10** and 4,4′-bis(3-thienyl)biphenyl (**14**)[9] as a byproduct were formed (Figure 3). Because both the desired product **10** and

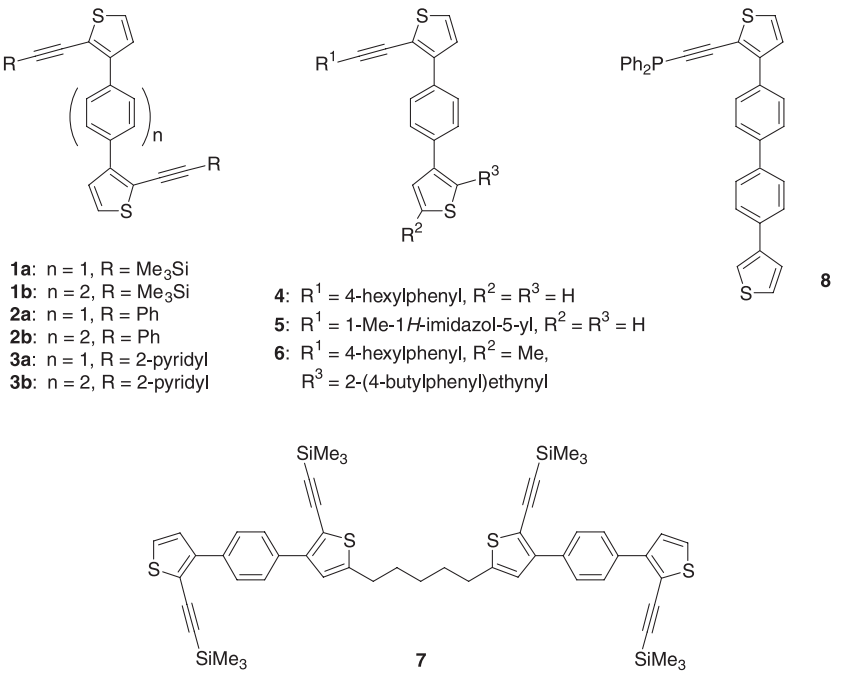


Figure 2 Structures of bisthienylarene derivatives.

the byproduct **14** were poorly soluble in common solvents, separation of **10** and **14** was difficult, and the crude product **10** was used in the following reaction: Iodination of a mixture of **10** and **14** with *N*-iodosuccinimide (NIS) afforded a mixture of 4-bromo-4′-(2-iodo-3-thienyl)biphenyl (**11**) and 4,4′-bis(2-iodo-3-thienyl)biphenyl (**15**)[9] in a 5:1 ratio. Both products turned out to be soluble in hexane, and they were separated by column chromatography to give pure **11** (46% yield based on 3-thiopheneboronic acid) and **15** (8% yield based on 4,4′-dibromobiphenyl).

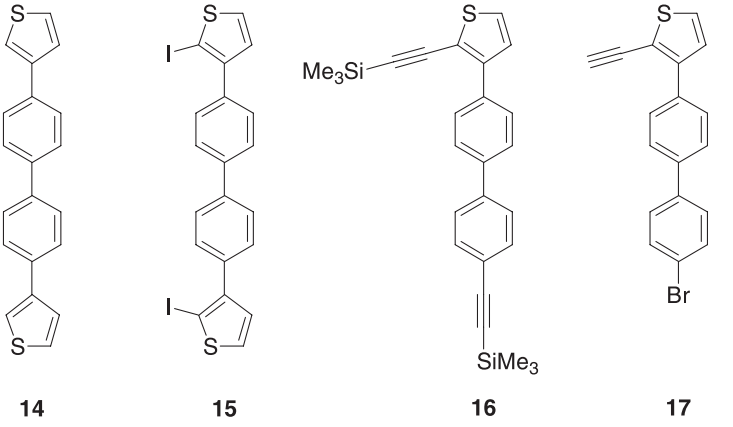
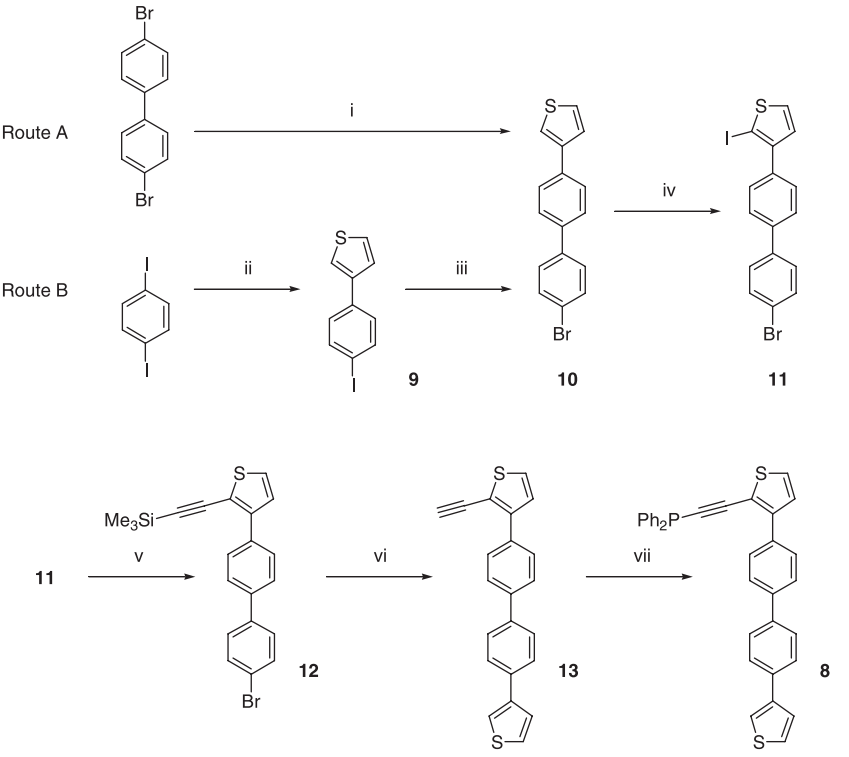


Figure 3 Structures of thienylbiphenyl derivatives.



Reagents: i, 3-thiopheneboronic acid, $Pd(PPh_3)_4$, PPh_3, K_3PO_4, 1,4-dioxane, H_2O; ii, 3-thiopheneboronic acid, $Pd(PPh_3)_4$, PPh_3, K_3PO_4, 1,4-dioxane, H_2O; iii, 4-bromophenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, toluene, THF, H_2O; iv, NIS, AIBN, AcOH, $CHCl_3$, v, ethynyltrimethylsilane, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF; vi, 3-thiopheneboronic acid, $Pd(PPh_3)_4$, PPh_3, K_3PO_4, H_2O, 1,4-dioxane; vii, EtMgBr, THF, then Ph_2PCl.

Scheme 1

On the other hand, in Route B, a Suzuki–Miyaura coupling reaction of 1,4-diiodobenzene with 3-thiopheneboronic acid at 75°C for 1.5 h afforded 1-iodo-4-(3-thienyl)benzene (**9**, 14% yield) and 1,4-bis(3-thienyl)benzene[12] (ca. 40% yield), along with a partial recovery of starting 1,4-diiodobenzene (44% recovery). This result indicates that compound **9** is more reactive than 1,4-diiodobenzene.

Compound **9** was then converted to **10** by cross-coupling with 4-bromophenylboronic acid. It should be noted that compound **10** was poorly soluble in hexane, while byproducts of this reaction were easily soluble in hexane. Thus, we obtained **10** in 81% yield after rinsing the crude product with hexane. Compound **10** was then reacted with NIS to give **11** in 74% yield. The total yield of **11** via Route B is 8% (based on 3-thiopheneboronic acid), while via Route A the total yield is 36%. Consequently Route A is better than Route B.[13]

After we obtained **11** by both Routes A and B, conversion of **11** to a substituted 4,4′-bis(3-thienyl)biphenyl derivative was examined. A Sonogashira coupling

of **11** with ethynyltrimethylsilane afforded 4-bromo-4′-[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]biphenyl (**12**) in 50% yield along with 4-[2-(trimethylsilyl)ethynyl]-4′-[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]biphenyl (**16**) in 23% yield. Compound **12** was then subjected to Suzuki–Miyaura coupling reaction with 3-thiopheneboronic acid. Under reaction conditions, coupling reaction and desilylation reaction took place and unsymmetrical compound **13** was obtained in 53% yield. Compound **17** was also obtained as a byproduct in 9% yield. Reaction of **13** with ethylmagnesium bromide followed by treatment with chlorodiphenylphosphine afforded the desired phosphine ligand **8** in 43% yield. ^{31}P NMR chemical shift of **8** [δ_P ($CDCl_3$) = –31.5] is close to that of the related species, $Ph_2PC{\equiv}CPh$ [δ_P (CH_2Cl_2) = –33.6].[14]

It should be mentioned that we have already prepared unsymmetrical ETB derivative **6** by reaction of 1-bromo-4-[2-{2-(4-hexylphenyl)ethynyl}-3-thienyl]benzene with 2-[2-{2-(4-butylphenyl)ethynyl}-5-methyl-3-thienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[10] Thus, preparation of unsymmetrical ETAr derivatives, containing two ethynyl groups, seems to be easy using **12** and appropriate 2-(2-ethynyl-3-thienyl)-1,3,2-dioxaborolane derivatives.

CONCLUSIONS

In summary, we have prepared unsymmetrical 4,4′-bis(3-thienyl)biphenyl derivatives, utilizing **11** as a key intermediate. A fundamental synthetic technique for building blocks of the linked ETAr system was developed, utilizing the chemistry of main group elements such as phosphorus, sulfur, and silicon. This rather simple preparative method of unsymmetrical ETAr-related species seems to help construction of sophisticated metal complex system (such as metalloprotein mimetics or artificial enzymes), containing $\sigma^3\lambda^3$- as well as $\lambda^3\sigma^2$-phosphorus atoms, the catalytic activities of which are of current interest.

EXPERIMENTAL

Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance-400 or AM-600, or a JEOL JNM-GSX400 spectrometer. UV-vis spectra were measured on a Hitachi U-3210 spectrometer, while a Shimadzu FTIR-8100M spectrometer was used to obtain the IR spectra. A Hitachi M-2500S spectrometer was used to obtain MS data. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer.

1-Iodo-4-(3-thienyl)benzene (9)

A mixture of 1,4-diiodobenzene (3.13 g, 9.50 mmol), 3-thiopheneboronic acid (1.02 g, 7.94 mmol), tetrakis(triphenylphosphine)palladium (93.9 mg, 0.08 mmol), triphenylphosphine (319 mg, 1.22 mmol), K_3PO_4 (5.01 g, 23.59 mmol), 1,4-dioxane (40 mL), and water (20 mL) was stirred at 75°C for 1.5 h. After cooling to room temperature, insoluble materials (1.10 g) containing 1,4-bis(3-thienyl)benzene were removed by filtration. The filtrate was worked up with chloroform (ca. 50 mL) and water (ca. 50 mL), and the organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (eluent = hexane) to give 322 mg (1.13 mmol, 14% yield based on the thiopheneboronic acid) of **9** and 1.39 g (44% recovery) of the starting 1,4-diiodobenzene.

Colorless powder, mp 150–152°C; $R_f = 0.38$ (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32$–7.35 (m, 3H, 4-thienyl, 3- and 5-phenyl), 7.39 (dd, $J = 5.0$, 2.9 Hz, 1H, 5-thienyl), 7.45 (dd, $J = 2.9$, 1.3 Hz, 1H, 2-thienyl), 7.72 (2H, 2- and 6-phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 92.3$ (1-phenyl), 120.6 (2-thienyl), 125.9 (4-thienyl), 126.5 (5-thienyl), 128.1 (3- and 5-phenyl), 135.2 (4-phenyl), 137.8 (2- and 6-phenyl), 141.1 (3-thienyl); IR (KBr): $\nu = 1902$, 1524, 1482, 1416, 1401, 1358, 1341, 1300, 1267, 1252, 1202, 1117, 1090, 1063, 1001, 893, 864, 828, 777, 704, 691, 629, 502 cm^{-1}; EI-MS (70 eV) *m/z* (rel. intensity): 286 (M^+; 100), 159 (M^+–I; 8). Found: *m/z* 285.9311. Calcd for $C_{10}H_7IS$: M, 285.9313. Found: C, 41.54; H, 2.62%. Calcd for $C_{10}H_7IS$: C, 41.98; H, 2.47%.

4-Bromo-4′-(3-thienyl)biphenyl (10)

Route A. A mixture of 4,4′-dibromobiphenyl (4.71 g, 15.1 mmol), 3-thiopheneboronic acid (2.00 g, 15.7 mmol), tetrakis(triphenylphosphine)palladium (135 mg, 0.117 mmol), triphenylphosphine (657 mg, 2.50 mmol), K_3PO_4 (16.1 g, 75.6 mmol), 1,4-dioxane (70 mL), and water (30 mL) was heated at 90°C for 5 h. After cooling to room temperature, the insoluble product was separated by filtration, and the solid was rinsed with hexane, collected by filtration, and dried to give 4.33 g of crude **10**, containing 4,4′-bis(3-thienyl)biphenyl (**14**) as a byproduct. This product was used in the following reaction in Route A without further purification.

Route B. A mixture of **9** (236 mg, 0.825 mmol), 4-bromophenylboronic acid (169 mg, 0.843 mmol), tetrakis(triphenylphosphine)palladium (14.4 mg, 0.012 mmol), K_2CO_3 (538 g, 2.53 mmol), 1,4-dioxane (40 mL), and water (20 mL) was heated at room temperature for 4.5 h and then at 75°C for 15 h. After cooling to room temperature, chloroform (ca. 50 mL) and water (ca. 50 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 rinsed with hexane and the resulting insoluble solid was collected by filtration. The solid was then washed with a small amount of chloroform and dried to give 210 mg (0.666 mmol, 81% yield) of **10**.

10: Colorless powder, mp 253–257°C; $R_f = 0.18$ (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.40$–7.44 (2H, m, 4- and 5-thienyl), 7.48–7.51 (3H, m, 2-thienyl and phenyl), 7.57 (2H, AA′BB′, phenyl), 7.59 (2H, AA′BB′, phenyl), and 7.68 (2H, AA′BB′, phenyl); IR (KBr) 1534, 1480, 1422, 1389, 1310, 1200, 1123, 1103, 1075, 1011, 1001, 968, 893, 864, 853, 820, 781, 733, 685, 671, 633, 552, 513, and 430 cm^{-1}; EI-MS (70 eV) *m/z* (rel intensity) 316 (M^++2; 100), 314 (M^+; 99), and 234 (M^+–Br–1; 12). Found: *m/z* 313.9761. Calcd for $C_{16}H_{11}BrS$: M, 313.9765. Found: C, 60.96; H, 3.52%. Calcd for $C_{16}H_{11}BrS$: C, 60.24; H, 3.74%. The ^{13}C NMR spectrum was not measured due to the low solubility.

4-Bromo-4′-(2-iodo-3-thienyl)biphenyl (11)

Route A. Crude 4-bromo-4′-(3-thienyl)biphenyl **10** was prepared as described above and used in the following reaction. A mixture of crude **10** (2.07 g, ca. 6.7 mmol), *N*-iodosuccinimide (NIS, 1.42 g, 6.30 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN, 101 mg, 0.615 mmol), and acetic acid (40 mL) in chloroform (60 mL) was stirred at 50°C for 3 h. Chloroform (ca. 60 mL) and water (ca. 80 mL) were added to the reaction mixture at room temperature, and the organic phase was treated with saturated aqueous $NaHCO_3$ and then saturated aqueous $Na_2S_2O_3$ solution. The organic phase was washed with brine,

dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with a silica-gel column chromatography (hexane:$CHCl_3$ 9:1) to give 1.52 g of **11** (3.44 mmol, ca. 52% yield from crude **10**; 46% theoretical yield based on the starting 3-thiopheneboronic acid) and 298 mg of 4,4′-bis(2-iodo-3-thienyl)biphenyl (**15**) (0.523 mmol, 8% theoretical yield based on the starting 4,4′-dibromobiphenyl).

Route B. A mixture of pure **10** (210 mg, 0.666 mmol), NIS (153 mg, 0.681 mmol), AIBN (19 mg, 0.12 mmol), and acetic acid (15 mL) in chloroform (20 mL) was stirred at 50°C for 3 h. Chloroform (ca. 20 mL) and water (ca. 30 mL) were added to the reaction mixture at room temperature, and the organic phase was treated with saturated aqueous $NaHCO_3$ and then saturated aqueous $Na_2S_2O_3$ solution. The organic phase was washed with brine, 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 218 mg of **11** (0.493 mmol, 74% yield).

11: Colorless powder, mp 131–133°C; $R_f = 0.25$ (SiO_2-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.00$ (1H, d, $J = 5.5$ Hz, 4-thienyl), 7.50–7.57 (3H, m, 5-thienyl and phenyl), and 7.58–7.64 (6H, m, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 73.1$ (2-thienyl), 121.7 (4-phenyl), 126.7 (phenyl), 128.6 (phenyl), 128.9 (4-thienyl), 129.2 (phenyl), 131.3 (5-thienyl), 131.9 (phenyl), 135.8 (4′-phenyl), 139.1 (phenyl), 139.4 (phenyl), and 146.0 (3-thienyl); IR (KBr) 1607, 1588, 1534, 1482, 1387, 1347, 1308, 1244, 1130, 1076, 1001, 963, 872, 851, 814, 752, 743, 712, 677, 650, 629, 619, 558, 502, and 477 cm^{-1}; EI-MS (70 eV) *m/z* (rel intensity) 442 (M^++2; 100), 440 (M^+; 97), and 234 (M^+–I–Br; 26). Found: *m/z* 439.8731. Calcd for $C_{16}H_{10}BrIS$: M, 439.8731. Found: C, 43.23; H, 2.56%. Calcd for $C_{16}H_{10}BrIS$: C, 43.56; H, 2.28%.

4-Bromo-4′-[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]biphenyl (12)

A mixture of **11** (503 g, 1.141 mmol), ethynyltrimethylsilane (240 μL, 1.70 mmol), dichlorobis(triphenylphosphine)palladium(II) (111 mg, 0.159 mmol), copper(I) iodide (23 mg, 0.12 mmol), and diisopropylamine (20 mL) in THF (30 mL) was stirred at 50°C for 24 h. After cooling to room temperature, chloroform (ca. 100 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was treated with a silica-gel column chromatography (hexane:chloroform = 9:1) to give 233 mg (0.567 mmol, 50% yield) of **12** and 112 mg (0.261 mmol, 23% yield based on **11**) of **16**.

12: Colorless solid, mp 134–136°C; $R_f = 0.53$ (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.26$ (9H, s, $SiMe_3$), 7.23 (1H, d, $J = 5.2$ Hz, 4-thienyl), 7.27 (1H, d, $J = 5.2$ Hz, 5-thienyl), 7.50 (2H, d, $J = 8.6$ Hz, 2- and 6-phenyl), 7.57–7.61 (2H+2H, m, phenyl), and 7.91 (2H, d, $J = 8.4$ Hz, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = -0.3$ ($SiMe_3$), 98.1 (C≡C), 101.8 (C≡C), 118.1 (2-thienyl), 121.6 (4-phenyl), 126.5 (4-thienyl), 126.7 (phenyl), 127.5 (5-thienyl), 128.3 (phenyl), 128.5 (phenyl), 131.8 (phenyl), 134.4 (4′-phenyl), 139.0 (phenyl), 139.5 (phenyl), and 144.5 (3-thienyl); IR (KBr) 2145 (C≡C), 1609, 1532, 1482, 1389, 1248, 1181, 1096, 1075, 1011, 1001, 880, 814, 764, 747, 723, 706, 675, 656, 646, 558, 492, and 432 cm^{-1}; EI-MS (70 eV) *m/z* (rel intensity) 412 (M^++2; 100), 410 (M^+; 91), 397 (M^+–Me+2; 50), 395 (M^+–Me; 47), and 301 (M^+–Br–2Me; 34). Found: *m/z* 410.0156. Calcd for $C_{21}H_{19}BrSSi$: M, 410.0160. Found: C, 60.27; H, 4.62%. Calcd for $C_{21}H_{19}BrSSi{\cdot}(H_2O)_{1/2}$: C, 59.99; H, 4.79%.

16: Colorless solid, mp 152–155°C; $R_f = 0.46$ (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.26$ (9H, s, $SiMe_3$), 0.27 (9H, s, $SiMe_3$), 7.23 (1H, d, $J = 5.3$ Hz, 4-thienyl),

7.27 (1H, d, J = 5.3 Hz, 5-thienyl), 7.55 (2H, AA′BB′, phenyl), 7.59 (2H, AA′BB′, phenyl), 7.63 (2H, AA′BB′, phenyl), and 7.91 (2H, AA′BB′, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = –0.3 ($SiMe_3$), –0.1 ($SiMe_3$), 94.9 (C≡C), 98.2 (C≡C), 101.8 (C≡C), 104.9 (C≡C), 118.0 (2-thienyl), 122.0 (4-phenyl), 126.5 (4-thienyl), 126.6 (phenyl), 126.8 (phenyl), 127.5 (5-thienyl), 128.2 (phenyl), 132.4 (phenyl), 134.4 (4′-phenyl), 139.3 (phenyl), 140.5 (phenyl), and 144.5 (3-thienyl); IR (KBr) 2157 (C≡C), 2143 (C≡C), 1491, 1250, 1094, 1003, 865, 840, 824, 758, and 725 cm^{-1}; EI-MS (70 eV) *m/z* (rel intensity) 428 (M^+; 100), 413 (M^+–Me; 41), and 73 (Me_3Si^+; 6). FT-ICR-MS Found: *m/z* 451.1342. Calcd for $C_{26}H_{28}NaSSi_2$: M^++Na, 451.1342.

4-(2-Ethynyl-3-thienyl)-4′-(3-thienyl)biphenyl (13)

A mixture of **12** (312 mg, 0.757 mmol), 3-thiopheneboronic acid (119 mg, 0.926 mmol), tetrakis(triphenylphosphine)palladium (14 mg, 0.012 mmol), triphenylphosphine (33 mg, 0.13 mmol), K_3PO_4 (863 mg, 4.06 mmol), 1,4-dioxane (80 mL), and water (20 mL) was heated at 80°C for 12 h. After cooling to room temperature, chloroform (ca. 100 mL) and water (ca. 100 mL) were added to the reaction mixture. The organic phase was 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 (CCl_4) to give 138 mg (0.40 mmol, 53% yield) of **13** and 24 mg (0.070 mmol, 9% yield) of **17**.

13: Pale yellow solid, mp 223–226°C (decomp); R_f = 0.39 (SiO_2-CCl_4); ^1H NMR (400 MHz, $CDCl_3$) δ = 3.47 (1H, s, C≡CH), 7.23 (1H, d, J = 5.3 Hz, 4-thienyl), 7.31 (1H, d, J = 5.3 Hz, 5-thienyl), 7.42 (1H, dd, J = 5.1 Hz and 2.9 Hz, 5′-thienyl), 7.45 (1H, dd, J = 5.1 Hz and 1.4 Hz, 4′-thienyl), 7.51 (1H, dd, J = 2.9 Hz and 1.4 Hz, 2′-thienyl), 7.69–7.71 (6H, m, phenyl), and 7.87 (2H, AA′BB′, phenyl); IR (KBr) 3287, 3100, 2095 (C≡C), 1528, 1491, 1431, 1418, 1401, 1202, 1088, 1001, 878, 864, 830, 781, 749, 727, 706, 671, 656, 631, 592, and 502 cm^{-1}; EI-MS (70 eV) *m/z* (rel intensity) 342 (M^+; 100). Found: *m/z* 342.0533. Calcd for $C_{22}H_{14}S_2$: M, 342.0537. ^{13}C NMR spectrum was not measured because of the poor solubility.

17: Pale yellow solid, mp 124–126°C (decomp); R_f = 0.52 (SiO_2-CCl_4); ^1H NMR (600 MHz, $CDCl_3$) δ = 3.46 (1H, s, C≡CH), 7.20 (1H, d, J = 5.3 Hz, 4-thienyl), 7.29 (1H, d, J = 5.3 Hz, 5-thienyl), 7.49 (2H, AA′BB′, phenyl), 7.57 (2H, AA′BB′, phenyl), 7.61 (2H, AA′BB′, phenyl), and 7.84 (2H, AA′BB′, phenyl); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 77.3 (C≡C), 83.7 (C≡C), 117.0 (2-thienyl), 121.7 (4-phenyl), 126.9 (thienyl), 127.0 (phenyl), 127.8 (thienyl), 128.4 (phenyl), 128.6 (phenyl), 131.9 (phenyl), 134.4 (*ipso*-phenyl), 139.2 (*ipso*-phenyl), 139.5 (*ipso*-phenyl), and 145.2 (3-thienyl); IR (KBr) 3287, 3104, 2095 (C≡C), 1586, 1480, 1428, 1389, 1125, 1078, 1011, 1001, 878, 855, 816, 781, 747, 725, 671, 656, 598, and 494 cm^{-1}; EI-MS (70 eV) *m/z* (rel intensity) 340 (M^++2; 100), 338 (M^+; 98), and 258 (M^+–Br–1; 54). Found: *m/z* 337.9760. Calcd for $C_{18}H_{11}BrS_2$: M, 337.9765.

4-[2-(2-Diphenylphosphinoethynyl)-3-thienyl]-4′-(3-thienyl)biphenyl (8)

To a solution of **13** (105 mg, 0.307 mmol,) in THF (20 mL), 0.32 mmol of ethylmagnesium bromide (1.0 mol/L solution in THF) was added, and the resulting mixture was stirred at 0°C for 30 min. Chlorodiphenylphosphine (0.06 mL, 0.32 mmol) was added to the mixture at 0°C, and the reaction mixture was stirred at room temperature for 1 h.

Chloroform (ca. 50 mL) and water (ca. 50 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 an alumina column chromatography ($CHCl_3$) to give 84 mg (0.14 mmol, 43% yield) of **8**.

8: Pale yellow solid, mp 181–183°C; $R_f = 0.57$ (Al_2O_3-CCl_4); ^{1}H NMR (600 MHz, CD_2Cl_2) $\delta = 7.21$ (1H, d, $J = 4.9$ Hz, 4-thienyl), 7.25–7.28 (6H, m, phenyl), 7.31 (1H, d, $J = 4.9$ Hz, 5-thienyl), 7.36 (1H, dd, $J = 4.7$ Hz and 2.9 Hz, 5′-thienyl), 7.40 (1H, dd, $J = 4.7$ Hz and 1.5 Hz, 4′-thienyl), 7.48 (1H, dd, $J = 2.9$ Hz and 1.5 Hz, 2′-thienyl), 7.52–7.56 (4H, m, phenyl), 7.55 (2H, AA′BB′, 2- and 6-biphenyl), 7.60 (2H, AA′BB′, 2′- and 6′-biphenyl), 7.64 (2H, AA′BB′, 3′- and 5′-biphenyl), and 7.78 (2H, AA′BB′, 3- and 5-biphenyl); ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2) $\delta = 91.8$ (d, $J_{PC} = 10.0$ Hz, C≡C), 100.2 (C≡C), 116.7 (2-thienyl), 119.6 (2′-thienyl), 125.4 (4′-thienyl), 125.7 (5′-thienyl), 126.0 (2-,6- or 3′-,5′-biphenyl), 126.1 (2-,6- or 3′-,5′-biphenyl), 126.5 (2′- and 6′-biphenyl), 127.0 (5-thienyl), 127.1 (4-thienyl), 127.7 (3- and 5-biphenyl), 127.9 (d, $^3J_{PC} = 7.2$ Hz, *m*-phenyl), 128.4 (*p*-phenyl), 131.9 (d, $^2J_{PC} = 20.0$ Hz, *o*-phenyl), 133.3 (4-biphenyl), 134.2 (4′-biphenyl), 135.1 (d, $^1J_{PC} = 7.2$ Hz, *ipso*-phenyl), 138.3 (1′-biphenyl), 139.1 (1-biphenyl), 140.9 (3′-thienyl), and 144.8 (3-thienyl); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = -31.5$; UV (CH_2Cl_2) 296 nm (log ε 4.54); IR (KBr) 2963, 2137 (C≡C), 1526, 1491, 1478, 1433, 1418, 1368, 1262, 1202, 1094, 1026, 1003, 876, 866, 828, 783, 749, 695, 633, 540, 513, and 451 cm^{-1}. FT-ICR-MS Found: *m/z* 549.0873. Calcd for $C_{34}H_{23}NaPS_2$: M+Na$^+$, 549.0876.

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