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PREPARATION OF 1,4-BIS(2-ETHYNYL-3-THIENYL)BENZENES AS VERSATILE SPACERS FOR CONNECTION OF HETEROCYCLES

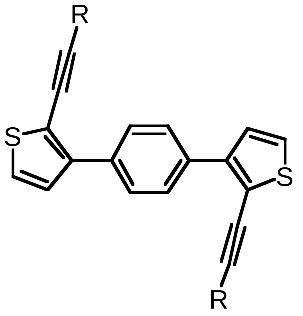
Kozo Toyota,* Yoichi Goto, Kazuyuki Okada, and Noboru Morita

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan; E-mail toyota@mail.tains.tohoku.ac.jp

Abstract – Iodination of 1,4-di(3-thienyl)benzene gave 1,4-bis(2-iodo-3-thienyl)-benzene, which was converted to 1,4-bis(2-ethynyl-3-thienyl)benzene. Novel 1,4-bis[2-(pyridylethynyl)-3-thienyl]benzene ligands containing the bis(ethynylthienyl)benzene spacer were prepared by Sonogashira reaction. Advantage of the spacer was demonstrated by introducing functionalized alkyl groups to the 5-position of the thiophene ring of 1,4-bis[2-(trialkylsilylethynyl)-3-thienyl]benzene.

INTRODUCTION

Thiophene spacers containing 2,5-thienylene moieties are of current interest.[1] In contrast, 2,3-thienylene moieties are rarely used as a spacer, probably because it does not construct linear-shape molecule such as molecular wire, which is currently of great interest. Nevertheless, the 2,3-thienylene spacer has an advantage: introduction of substituents or functional groups into the 5-position of the thiophene ring is easy. This advantage will help, for example, researches on sophisticated ligands. In the course of our continuing researches on developing novel ligands and homogeneous catalysts,[2] we interested in the ligand system containing the 2,3-thienylene spacer. We now report here preparation of 1,4-bis(2-ethynyl-3-thienyl)benzene (**1**) and its application to preparation of pyridine derivatives **2** as well as **3** (Chart 1), in which the bis(ethynylthienyl)benzene moiety is incorporated as a spacer (hereafter abbreviated to the ETB spacer).[3]

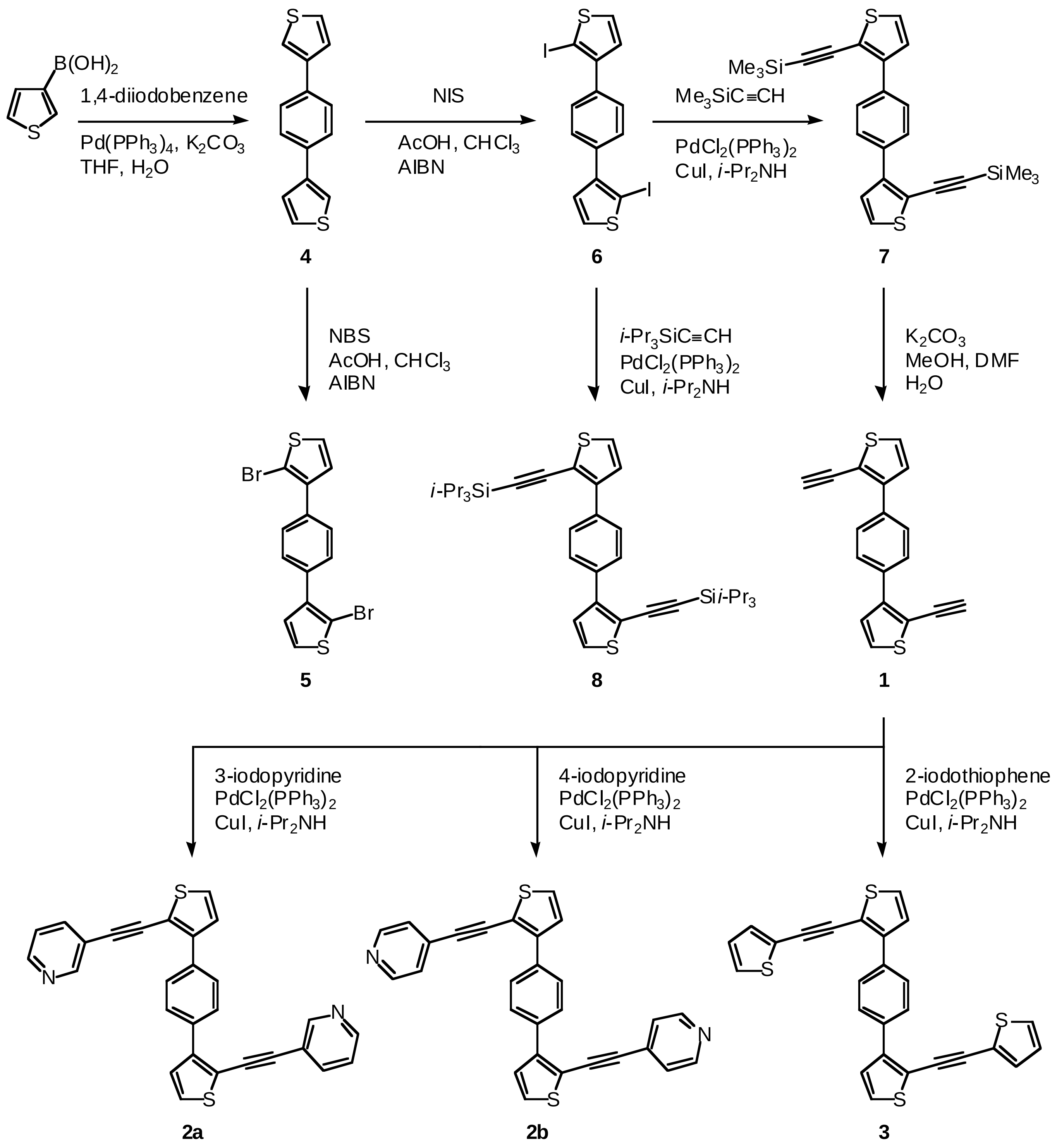


1: R = H
2a: R = 3-pyridyl
2b: R = 4-pyridyl
3: R = 2-thienyl

Chart 1

RESULTS AND DISCUSSION

In the literature, 1,4-di(3-thienyl)benzene (**4**) was prepared starting from 1,4-di(3-thienyl)-1,3-butadiene and diethyl acetylenedicarboxylate.[4,5] In the present study, however, the starting material **4** was prepared (92% yield) by Suzuki coupling between 1,4-diiodobenzene and 3-thiophene boronic acid (Scheme 1). Selective halogenation of the 2-position (of the thiophene ring of **4**) was achieved by using NBS or NIS in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN) to give **5** (90% yield) or **6** (67% yield), respectively. It should be noted that compounds **5** and **6** are not so stable in air and the yields depend on the work up conditions including column chromatography. Trialkylsilylethynyl groups were then introduced to the diiodo derivative **6** by Sonogashira reaction with ethynyltrimethylsilane or ethynyltriisopropylsilane to give **7** (96% yield) or **8** (76% yield), respectively. Desilylation of **7** with potassium carbonate afforded the unsubstituted ETB spacer, 1,4-bis(2-ethynyl-3-thienyl)benzene (**1**) in 96% yield. Thus, each step of the preparation of **1** proceeded with good yield.



Scheme 1

In order to evaluate the effect of the ETB spacer, it was applied to 3,3’- or 4,4’-bipyridyl system. Sonogashira reaction of **1** with 3-iodopyridine or 4-iodopyridine afforded the bis(pyridylethynylthienyl)benzenes **2a** (68% yield) or **2b** (76% yield), respectively. Compound **3** was also obtained in 52% yield by a similar reaction of **1** with 2-iodothiophene.

Figure 1 shows UV-vis spectra of **1**–**3**. Compounds **2a**,**b** and **3** show relatively similar absorption spectra, which shifted to the longer wavelength than that of **1** with larger molar absorption coefficients. The absorption spectrum of **3** exhibits bathochromic shift compared to the spectrum of 1,2-di(2-thienyl)ethyne [λ_{max} (CH_2Cl_2) ca. 315 nm (ε ca. 23000)],[6] this may indicate considerable contribution of conjugation through the benzene ring of **3**. Situation seems to be similar in the case of **2a** and 3-[(2-thienyl)ethynyl]pyridine [λ_{max} (hexane) 286 (ε 15000), 302 (19100), 308 (16500), and 320 nm (16300)].[7]

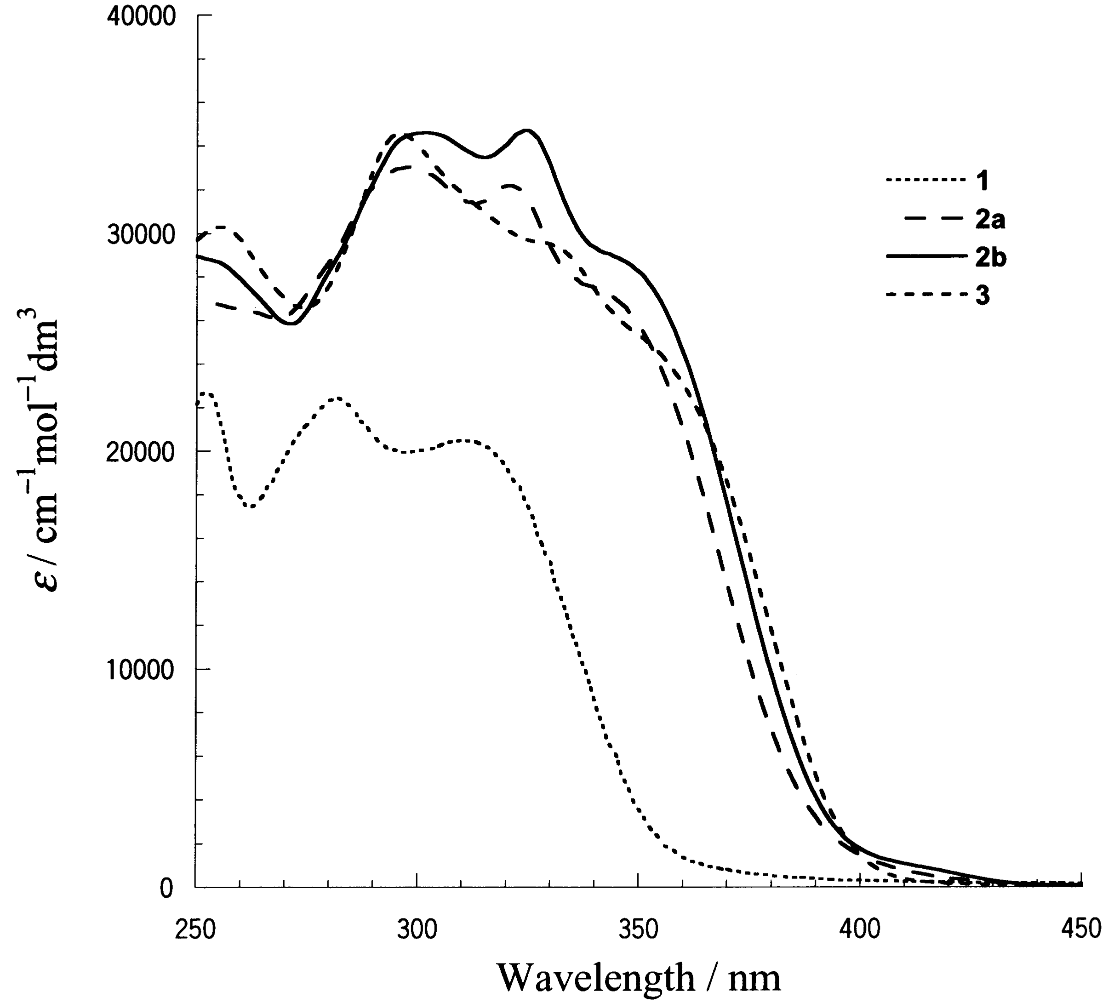
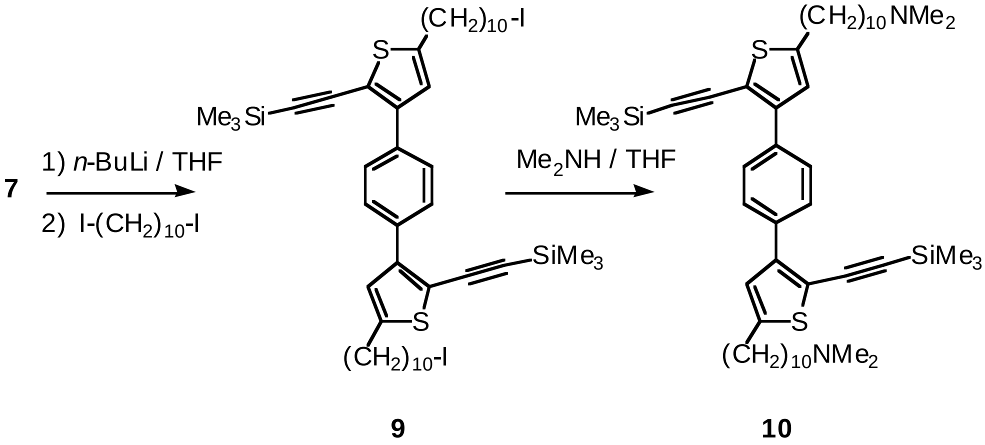


Figure 1. UV-vis spectra of **1**, **2a**,**b**, and **3** in CH_2Cl_2.

Advantage of the ETB spacer was then demonstrated by introducing functionalized alkyl groups to the 5-position of the thiophene ring as follows. Lithiation of **7** with butyllithium followed by reaction with 1,10-diiodododecane afforded bis(iododecyl) derivative **9** in ca. 40% yield (Scheme 2). Compound **9** is a promising building block for various functional group-substituted ETB spacers. In fact, dimethylamino group was introduced by treatment of **9** with dimethylamine-THF solution to give **10** (12% overall yield based on the starting **7**).



Scheme 2

In conclusion, we have prepared new ETB spacers **1** and **3**, as well as the useful intermediate **9**. These compounds seem to be promising synthetic intermediates for various functionalized ligands. They may be also applicable to preparations of some 'accumulated' transition-metal complexes, which are of current interest. Studies on such ligands and their complexes are now in progress.

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. IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on a Hitachi M-2500S spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer.

1,4-Di(3-thienyl)benzene (4). A mixture of 1,4-diiodobenzene (500 mg, 1.52 mmol), 3-thiopheneboronic acid (500 mg, 3.95 mmol), tetrakis(triphenylphosphine)palladium (117 mg, 0.11 mmol), K_2CO_3 (2.10 g, 15.2 mmol), toluene (10 mL), THF (10 mL), and water (5 mL) was heated at 85 °C for 24 h. Precipitates were collected by filtration and washed with hexane to give **4** (340.2 mg, 1.40 mmol) in 92% yield. **4**: Colorless scales, mp 281–282 °C (sublimation occurred below mp; lit.[4] 274 °C), $R_f = 0.39$ (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.37$–7.49 (6H, AA'B, thienyl) and 7.63 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 120.2$ (2-thienyl), 126.2 (4- or 5-thienyl), 126.3 (4- or 5-thienyl), 126.8 (2-,3-,5-, and 6-phenyl), 134.6 (1- and 4-phenyl), and 141.9 (3-thienyl).

1,4-Bis(2-bromo-3-thienyl)benzene (5). A mixture of **4** (37.3 mg, 0.153 mmol), *N*-bromosuccinimide (59.6 mg, 0.335 mmol), AIBN (2.5 mg, 0.015 mmol), and AcOH (1 mL) in $CHCl_3$ (5 mL) was stirred at 50 °C for 5 h. The resulting mixture was treated with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ solution. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was treated with a short silica-gel column chromatography (CCl_4) to give 55.2 mg (0.138 mmol, 90% yield) of **5**: Colorless scales, mp 175–178 °C (decomp); R_f 0.44 (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.08$ (2H, d, $J = 5.6$ Hz, 4-thienyl), 7.32 (2H, d, $J = 5.6$ Hz, 5-thienyl), and 7.63 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 108.7$ (C-Br), 126.0 (4-thienyl), 128.6 (2-,3-,5-, and 6-phenyl), 129.0 (5-thienyl), 134.2 (1- and 4-phenyl), and 140.6 (3-thienyl); IR (KBr) 1496, 1425, 1404, 1336, 1200, 980, 864. 839, 823, 717, 629, and 538 cm^{-1}; Found: *m/z* 398.8420. Calcd for $C_{14}H_8Br_2S_2$: M, 397.8434. This compound gradually decomposed in air.

1,4-Bis(2-iodo-3-thienyl)benzene (6). A mixture of **4** (1.20 g, 4.94 mmol), *N*-iodosuccinimide (2.78 g, 12.4 mmol), AIBN (70 mg, 0.43 mmol), and AcOH (10 mL) in $CHCl_3$ (20 mL) was stirred at 50 °C for 5 h. The resulting mixture was treated with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ 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 (hexane-$CHCl_3$ 50:1) to give 1.63 g (3.30 mmol, 67% yield) of **6**: Colorless scales, mp 126–128 °C (decomp); $R_f = 0.46$ (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.01$ (2H, d, $J = 5.6$ Hz, 4-thienyl), 7.51 (2H, d, $J = 5.6$ Hz, 5-thienyl), and 7.59 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 73.0$ (C-I), 128.7 (2-,3-,5-, and 6-phenyl),129.0 (4-thienyl), 131.3 (5-thienyl), 135.7 (1- and 4-phenyl), and 146.1 (3-thienyl); IR (KBr) 1491, 1335, 955, 860. 839, 717, 633, and 546 cm^{-1}; Found: *m/z* 493.8157. Calcd for $C_{14}H_8I_2S_2$: M, 493.8157. This compound gradually decomposed in air.

1,4-Bis[2-(trimethylsilylethynyl)-3-thienyl]benzene (7). A mixture of **6** (673 mg, 1.36 mmol), ethynyltrimethylsilane (0.48 mL, 3.4 mmol), dichlorobis(triphenylphosphine)palladium(II) (134 mg, 0.19 mmol), copper(I) iodide (18.1 mg, 0.10 mmol), and diisopropylamine (1.5 mL) in THF (20 mL) was stirred at 50 °C for 24 h. To the resulting mixture were added $CHCl_3$ and water. 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 (hexane-$CHCl_3$ 20:1) to give 570 mg (1.31 mmol, 96% yield) of **7**: Pale yellow prisms, mp 133–134 °C (decomp); $R_f = 0.43$ (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.24$ (18H, s, $SiMe_3$), 7.23 (2H, d, $J = 5.3$ Hz, thienyl), 7.25 (2H, d, $J = 5.3$ Hz, thienyl), and 7.88 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = -0.21$ ($SiMe_3$), 98.3 (C≡C), 101.9 (C≡C), 118.0 (2-thienyl), 126.5 (thienyl), 127.6 (thienyl), 127.7 (2-,3-,5-, and 6-phenyl), 134.3 (1- and 4-phenyl), and 144.6 (3-thienyl); UV (CH_2Cl_2) 259 (log ε 4.46), 289 (4.45), and 327 nm (4.38); IR (KBr) 2962, 2951, 2141, 1496, 1433, 1246, 1173, 1120, 1086, 845, 756, 721, and 652 cm^{-1}; Found: *m/z* 457.0905. Calcd for $C_{24}H_{26}NaS_2Si_2$: M^++Na 457.0907. Anal. Calcd for $C_{24}H_{26}S_2Si_2 \bullet H_2O$: C, 63.76; H, 6.23%. Found: C, 64.02; H, 5.98%.

1,4-Bis[2-(triisopropylsilylethynyl)-3-thienyl]benzene (8). A mixture of **6** (1.50 g, 3.04 mmol), ethynyltriisopropylsilane (1.7 mL, 7.60 mmol), dichlorobis(triphenylphosphine)palladium(II) (320 mg, 0.46 mmol), copper(I) iodide (58 mg, 0.30 mmol), and diisopropylamine (3.4 mL) in THF (15 mL) was stirred at 50 °C for 24 h. To the resulting mixture were added $CHCl_3$ and water. 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 (hexane-$CHCl_3$ 50:1) to give 1.4 g (2.32 mmol, 76% yield) of **8**: Pale yellow powder, mp 115–116 °C (CH_2Cl_2-MeOH); R_f 0.41 (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.09$ (6H, br s, C*H*Me$_2$), 1.10 (36H, br s, CH*Me*$_2$), 7.20 (2H, d, $J = 5.3$ Hz, thienyl), 7.24 (2H, d, $J = 5.3$ Hz, thienyl), and 7.85 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 11.3$ (*C*HMe$_2$), 18.7 (CH*Me*$_2$), 98.6 (C≡C), 99.7 (C≡C), 118.5 (2-thienyl), 126.2 (thienyl), 127.6 (thienyl), 127.8 (2-,3-,5-, and 6-phenyl), 134.3 (1- and 4-phenyl), and 144.4 (3-thienyl); UV (CH_2Cl_2) 260 (log ε 4.46), 289 (4.44), and 327 nm (4.38); IR (KBr) 2943, 2864, 2139, 1462, 1068, 1020, 995, 883, 764, 723, 675, and 660 cm^{-1}; Found: *m/z* 625.2783. Calcd for $C_{36}H_{50}NaS_2Si_2$: M$^+$+Na, 625.2785. Anal. Calcd for $C_{36}H_{50}S_2Si_2 \bullet (H_2O)_{1/2}$: C, 70.64; H, 8.40%. Found: C, 70.61; H, 8.27%.

1,4-Bis(2-ethynyl-3-thienyl)benzene (1). A mixture of **7** (100 mg, 0.230 mmol), K_2CO_3 (80 mg, 0.58 mmol), MeOH (3 mL), DMF (2 mL), and water (1.5 mL) was stirred at rt for 3 h. The mixture was extracted using $CHCl_3$ and water, 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 (hexane-EtOAc 1:1) to give 64.0 mg (0.220 mmol, 96% yield) of **1**: Yellow powder, mp 115–117 °C (decomp); $R_f = 0.37$ (SiO_2-CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 3.45$ (2H, s, C≡CH), 7.21 (2H, d, $J = 5.3$ Hz, thienyl), 7.29 (2H, d, $J = 5.3$ Hz, thienyl), and 7.83 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) $\delta = 76.8$ (C≡C), 83.4 (C≡C), 116.6 (2-thienyl), 126.7 (4- or 5-thienyl), 127.6 (4- or 5-thienyl), 127.7 (2-,3-,5-, and 6-Ph), 134.1 (1- and 4-Ph), and 145.0 (3-thienyl); UV (CH_2Cl_2) 252 (log ε 4.36), 282 (4.35), and 310 nm (4.31); IR (KBr) 3288, 3103, 2922, 2094, 872, 849, 731, 663, 594, and 507 cm^{-1}. Found: *m/z* 313.0116. Calcd for $C_{18}H_{10}NaS_2$: M$^+$+Na, 313.0116. Anal. Calcd for $C_{18}H_{10}S_2 \bullet (H_2O)_{1/2}$: C, 72.21; H, 4.04%. Found: C, 71.79; H, 3.84%.

1,4-Bis[2-(3-pyridylethynyl)-3-thienyl]benzene (2a). A mixture of **1** (300 mg, 1.00 mmol), 3-iodopyridine (614 mg, 3.00 mmol), dichlorobis(triphenylphosphine)palladium(II) (70 mg, 0.10 mmol), copper(I) iodide (1.9 mg, 0.010 mmol), and diisopropylamine (1.2 mL) in THF (10 mL) was stirred at 50 °C for 24 h. To the resulting mixture were added $CHCl_3$ and water. 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 (EtOAc) to give 300 mg (0.68 mmol, 68% yield) of **2a**: Yellow powder, mp 183–186 °C (decomp); $R_f = 0.39$ (SiO_2-EtOAC); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.18$ (2H, dd, $J = 8.0$ Hz and $J = 4.8$ Hz, 5-pyridyl), 7.24 (2H, d, $J = 5.4$ Hz, thienyl), 7.32 (2H, d, $J = 5.4$ Hz, thienyl), 7.67 (2H, br d, 4-pyridyl), 7.88 (4H, s, phenyl), 8.49 (2H, br d, 6-pyridyl), and 8.68 (2H, br s, 2-pyridyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 86.6$ (C≡C), 91.8 (C≡C), 117.3 (2-thienyl), 120.1 (3-

pyridyl), 123.0 (5-pyridyl), 127.4 (thienyl), 127.9 (thienyl, 2-,3-,5-, and 6-phenyl), 134.5 (1- and 4-phenyl), 137.9 (4-pyridyl), 144.8 (3-thienyl), 148.5 (6-pyridyl), 151.7 (2-pyridyl); UV (CH_2Cl_2) 298 (log ε 4.52), 320 (4.51), and 346 nm (sh, 4.43); IR (KBr) 2197, 1554, 1498, 1473, 1433, 1398, 1022, 872, 847, 808, 739, 706, 652, 627, and 528 cm^{-1}; Found: *m/z* 467.0648. Calcd for $C_{28}H_{16}N_2NaS_2$: M^++Na, 467.0647. Anal. Calcd for $C_{28}H_{16}N_2S_2$• $(H_2O)_{1/2}$: C, 74.14; H, 3.78; N, 6.18%. Found: C, 74.05; H, 4.09; N, 5.95%.

1,4-Bis[2-(4-pyridylethynyl)-3-thienyl]benzene (2b). A mixture of **1** (105.4 mg, 0.363 mmol), 4-iodopyridine (221.9 mg, 1.08 mmol), dichlorobis(triphenylphosphine)palladium(II) (24.6 mg, 0.035 mmol), copper(I) iodide (8.0 mg, 0.042 mmol), and diisopropylamine (0.4 mL) in THF (3 mL) was stirred at 50 °C for 10 h. To the resulting mixture were added $CHCl_3$ and water. 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 (EtOAc) to give 123.3 mg (0.277mmol, 76% yield) of **2b**: Yellow powder, mp 179–182 °C (decomp); R_f = 0.26 (SiO_2-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (4H, d, J = 5.7 Hz, 3,5-pyridyl), 7.30 (2H, d, J = 5.3 Hz, thienyl), 7.42 (2H, d, J = 5.3 Hz, thienyl), 7.90 (4H, s, phenyl), and 8.54 (4H, d, J = 5.7 Hz, 2,6-pyridyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 88.0 (C≡C), 92.6 (C≡C), 117.0 (2-thienyl), 124.9 (3- and 4-pyridyl), 128.1 (thienyl, 2-,3-,5-, and 6-phenyl), 128.2 (thienyl), 131.0 (4-pyridyl), 134.6 (1- and 4-phenyl), 145.7 (3-thienyl), and 149.7 (2- and 6-pyridyl); UV (CH_2Cl_2) 301 (log ε 4.54), 324 (4.54), and 347 nm (sh, 4.46); IR (KBr) 2200, 1593, 1535, 1489, 1431, 1408, 1213, 872, 818, 731, and 542 cm^{-1}; Found: *m/z* 467.0648. Calcd for $C_{28}H_{16}N_2NaS_2$: M^++Na, 467.0647. Anal. Calcd for $C_{28}H_{16}N_2S_2$• $(H_2O)_{1/2}$: C, 74.14; H, 3.78; N, 6.18%. Found: C, 74.04; H, 3.83; N, 5.89%.

1,4-Bis[2-{2-(2-thienyl)ethynyl}-3-thienyl]benzene (3). A mixture of **1** (50 mg, 0.17 mmol), 2-iodothiophene (76 mg, 0.36 mmol), dichlorobis(triphenylphosphine)palladium(II) (11.7 mg, 0.017 mmol), copper(I) iodide (0.3 mg, 0.002 mmol), and diisopropylamine (0.2 mL) in THF (1.7 mL) was stirred at 50 °C for 24 h. To the resulting mixture were added $CHCl_3$ and water. 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 (hexane-EtOAc 40:1) to give 40 mg (0.088 mmol, 52% yield) of **3** along with 6.2 mg (0.021 mmol) of **1** (12% recovery). **3**: Yellow powder, mp 132–133 °C; R_f = 0.36 (SiO_2-CCl_4); ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.00 (2H, dd, ^3J = 5.2 Hz and ^3J = 3.6 Hz, thienyl), 7.26 (2H, dd, ^3J = 3.6 Hz and ^4J = 1.2 Hz, thienyl), 7.32 (2H, d, ^3J = 5.4 Hz, thienyl), 7.32 (2H, dd, ^3J = 5.2 Hz and ^4J = 1.2 Hz, thienyl), 7.39 (2H, d, ^3J = 5.4 Hz, thienyl), and 7.92 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 86.9 (C≡C), 88.6 (C≡C), 117.8 (2-thienyl), 123.0 (thienyl), 126.9 (thienyl), 127.1 (thienyl), 127.6 (thienyl), 127.89 (thienyl), 127.94 (2-,3-,5-, and 6-phenyl), 132.0 (thienyl), 134.5 (1- and 4-phenyl), and 144.3 (3-thienyl); UV (CH_2Cl_2) 255 (log ε 4.48), 296 (4.54), 333 (sh, 4.47), and 359 nm (sh, 4.37); IR (KBr) 1200, 1084, 1026, 870, 847, 827, 727, and 704 cm^{-1}; Found: *m/z* 476.9870. Calcd for

$C_{26}H_{14}NaS_4$: M^++Na, 476.9871. Anal. Calcd for $C_{26}H_{14}S_4$• $(H_2O)_{1/2}$: C, 67.35; H, 3.26%. Found: C, 67.32; H, 3.76%.

1,4-Bis[5-(10-iodododecyl)-2-(trimethylsilylethynyl)-3-thienyl]benzene (9). To a solution of **7** (1.35 g, 3.11 mmol) in THF (20 mL) was added 5.8 mL (9.3 mmol) of *n*-BuLi (1.6 M solution in hexane, M = mol / dm^3) at –78 °C and the resulting mixture was stirred for 15 min. The mixture was added to a THF (30 mL) solution of 1,10-diiododecane (11.5 g, 29.2 mmol) at 50 °C and the reaction mixture was stirred at 50 °C for 3 h. The mixture was extracted using $CHCl_3$ and water, 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 (hexane-$CHCl_3$ 20:1) to give 1.20 g (1.24 mmol, ca. 40% yield) of crude **9**: ^1H NMR (400 MHz, $CDCl_3$) δ = 0.36 (18H, s, $SiMe_3$), 1.20–1.50 (24H, m, CH_2), 1.60 (4H, m, thienyl-CH_2CH_2), 1.80 (4H, m, CH_2CH_2-I), 2.46 (4H, t, J = 6.8 Hz, thienyl-CH_2), 3.17 (4H, t, J = 7.6 Hz, CH_2-I), 7.31 (2H, s, 4-thienyl), and 7.84 (4H, s, phenyl). Found: *m/z* 989.1966. Calcd for $C_{44}H_{64}I_2NaS_2Si_2$: M^++Na, 989.1970.

1,4-Bis[5-(10-dimethylaminodecyl)-2-(trimethylsilylethynyl)-3-thienyl]benzene (10). To a solution of crude **9** (1.20 g, 1.24 mmol) in THF (20 mL) was added 6.2 mL (12.4 mmol) of dimethylamine (2 M solution in THF) at –78 °C and the resulting mixture was stirred 50 h at rt. The mixture was extracted using $CHCl_3$ and water, the organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with short ODS column chromatography (Nacalai Tesque Cosmosil 75C_{18}-PREP / EtOAc) and the crude product was further purified by an ODS column chromatography (Nacalai Tesque Cosmosil 40C_{18}-PREP / EtOAc) to give 0.295 g (0.368 mmol, 12% overall yield based on **7**) of **10**: Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.33 (18H, s, $SiMe_3$), 1.25 (20H, br s, CH_2), 1.42 (8H, br s, CH_2), 1.58 (4H, quin, ^3J = 7.2 Hz, CH_2), 2.20 (12H, s, NMe), 2.22 (4H, t, ^3J = 7.7 Hz, NCH_2), 2.43 (4H, t, ^3J = 7.0 Hz, thienyl-CH_2), 7.28 (2H, s, 4-thienyl), and 7.81 (4H, s, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = –0.21 ($SiMe_3$), 20.0 (CH_2), 27.0–30.0 (CH_2), 44.8 (NMe), 59.4 (NCH_2), 74.2 (C≡C), 98.0 (C≡C), 124.2 (2-thienyl), 127.7 (2-,3-,5-, and 6-phenyl), 134.3 (thienyl or phenyl), 134.4 (thienyl or phenyl), 141.0 (5-thienyl), and 144.2 (3-thienyl); IR (neat) 2929, 2854, 2814, 2762, 2141, 1458, 1250, 999, 841, and 758 cm^{-1}; Found: *m/z* 801.5059. Calcd for $C_{48}H_{77}N_2S_2Si_2$: M^++H, 801.5061.

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