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Preparations of bis[2-(2-arylethynyl)-3-thienyl]arenes and bis[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]arenes☆

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ABSTRACT

4,4′-Bis[2-(2-phenylethynyl)-3-thienyl]biphenyl, 4,4′-bis[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]biphenyl and their congeners were prepared and their properties were studied. Extension of π-system through the central benzene ring was suggested by UV–vis spectra. Connection of two 1,4-bis[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]benzene units was exemplified.

1. Introduction

Artificial molecular architecture is of current interest.[1] This category includes compounds so-called bio-mimetic or bio-inspired molecules, which resembles (from particular point of view concerning to the structure and functionality) to bio-polymers such as peptides, proteins, and so on. In the course of our continuing research on developing novel phosphorus ligands,[2] as well as their transition-metal complexes[3] and homogeneous catalysts,[4] the author (K.T.) was inspired by structures of metalloproteins and designed 1,4-bis(2-ethynyl-3-thienyl)benzene spacer (hereafter abbreviated to the ETB spacer). The ETB spacer is a promising and easily tunable spacer,[5] which has a 1,4-phenylene axis and a pair of 3-thienyl moieties[6] at the both ends of the axis. The spacer also has the ethynyl side chains on the thiophene rings. The ETB system and related systems [such as 4,4′-bis(2-ethynyl-3-thienyl)biphenyls[7]] may be applicable to construction of accumulated (or assembled) transition-metal complex systems such as artificial enzymes or metalloprotein-inspired molecules[8] (general structure is shown as **A** in Chart 1).

In the previous paper,[5] we have reported a preparation of compounds **1** and **2** (Chart 1) as well as conversion of **1** to pyridyl ligands **3b**,**c**. Characteristics of the ETB spacer are easy and selective introduction of substituents at the terminal sp carbon and/or 5-position of the thiophene rings, this advantage was exemplified by preparation of compounds **4** and **5**.[5] Compounds **4** and **5** have 1,4-bis(5-alkyl-3-thienyl)benzene backbone and multiple ethynyl side chains, which are fundamental forms of the ETB-linked systems such as **A** in Chart 1.

In order to progress the investigation of the ETB spacer-linked compounds, establishment of fundamental synthetic technique and evaluation of electronic properties of the spacer moieties are necessary. We report here preparation and properties of 1,4-bis[2-(2-phenylethynyl)-3-thienyl]benzene and its congeners, which will help evaluation of the ETB spacer.[9]

2. Results and discussion

2.1. Preparation of 1,4-bis[2-(2-phenylethynyl)-3-thienyl]benzene and related compounds

In the previous paper, we prepared 1,4-bis[2-(heteroarylethynyl)-3-thienyl]benzenes by Sonogashira reaction of **1** with heteroaryl iodide.[5] This time, however, compounds **3a** and **7a** were prepared from 1,4-bis(2-iodo-3-thienyl)benzene (**6**)[5] (Scheme 1). For the purpose of comparison of properties, 3-phenyl-2-ethynylthiophene derivatives **8**–**10** as well as 2-(2-phenylethynyl)thiophene (**11**)[10] were also prepared by a similar manner. Compound **3a** is soluble in chloroform, however, the phenylethynyl derivative **7a** is hardly soluble in chloroform (compound **7a** turned out to be soluble in DMSO). Thus, alkyl-substituted derivatives **7b**,**c**

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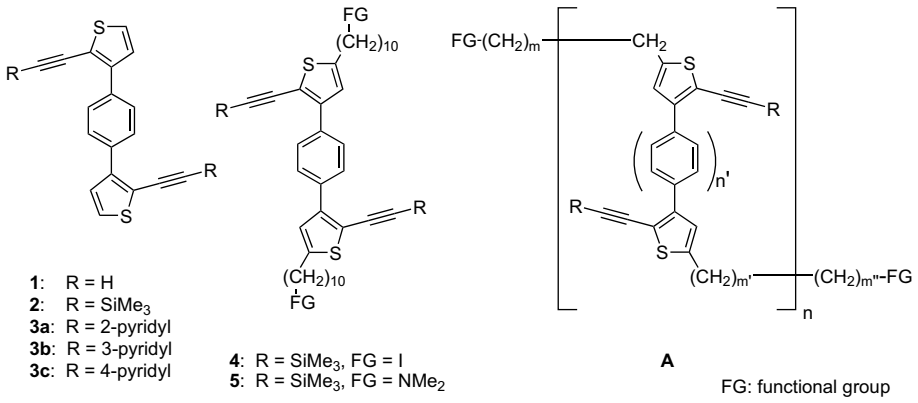
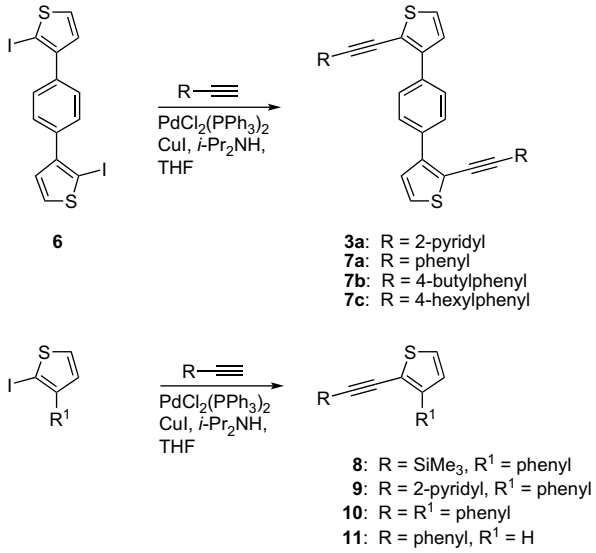


Chart 1.

were prepared. Fortunately, compounds **7b**,**c** turned out to be soluble in many solvents such as chloroform, dichloromethane, benzonitrile, or tetrahydrofuran (THF), although the solubility in hexane or acetonitrile is not very good.[11]



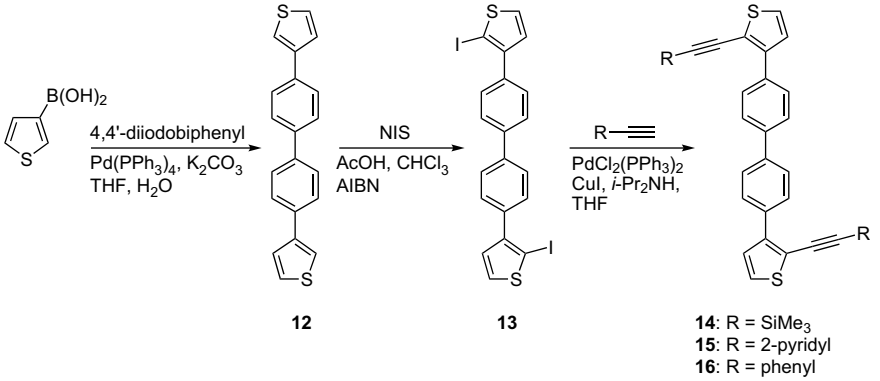
Scheme 1.

2.2. Preparation of 4,4′-bis[2-(2-arylethynyl)-3-thienyl]biphenyl derivatives

4,4′-Bis(2-ethynyl-3-thienyl)biphenyl derivatives were also prepared by a method similar to those of **3a** and **7a–c** (Scheme 2): Suzuki coupling of 4,4′-diiodobiphenyl with 3-thiopheneboronic acid gave 4,4′-di(3-thienyl)biphenyl (**12**), which was halogenated by *N*-iodosuccinimide (NIS) to form **13**. It should be noted that **12** was insoluble in common solvent and the iodination of **12** was carried out in suspension. Because **13** is more soluble than **12**, the iodination reaction tends to afford a mixture of **13** and over-iodinated products as well as the starting **12**; separation of **13** from by-products by silica-gel column chromatography turned out to be difficult. When 0.5 molar ratio (i.e., 0.25 equiv for diiodination) of NIS was used, **13** was successfully isolated in ca. 10% yield (41% yield based on NIS). However, from practical reason, crude **13** (obtained from reaction of **12** with 2 molar ratio of NIS) was used as a starting material in the following experiments: Sonogashira reaction of crude **13** with ethynyltrimethylsilane, 2-ethynylpyridine, or ethynylbenzene afforded **14–16**, respectively.

2.3. UV–vis spectra of 1,4-bis[2-(arylethynyl)-3-thienyl]benzenes

Figure 1 shows UV–vis spectra of parent spacer **1**, trimethylsilyl-substituted derivatives **2**, **8**, and **14**, as well as 4-butylphenyl congener **7b** in CH_2Cl_2. Bathochromic shifts were observed among the ETB derivatives in the order of **7b**>**2**>**1**, as expected. Compared to **8**, compound **2** shows significant red shift and increase of molar absorption coefficient, which indicates existence of significant



Scheme 2.

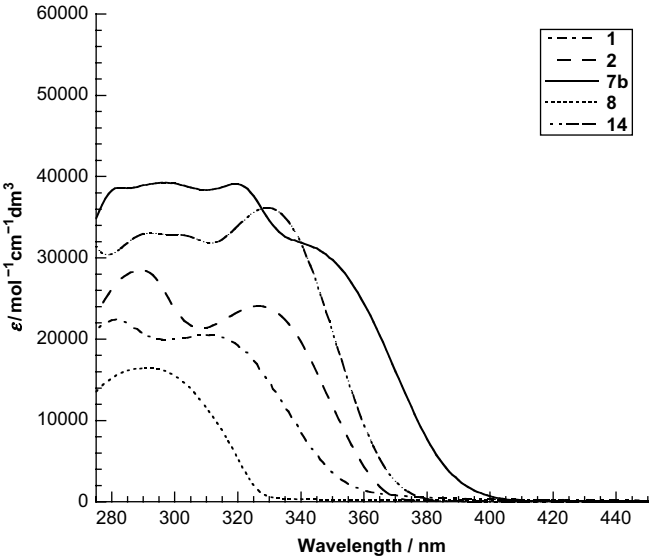


Figure 1. UV–vis spectra of **1**, **2**, **7b**, **8**, and **14** in CH_2Cl_2.

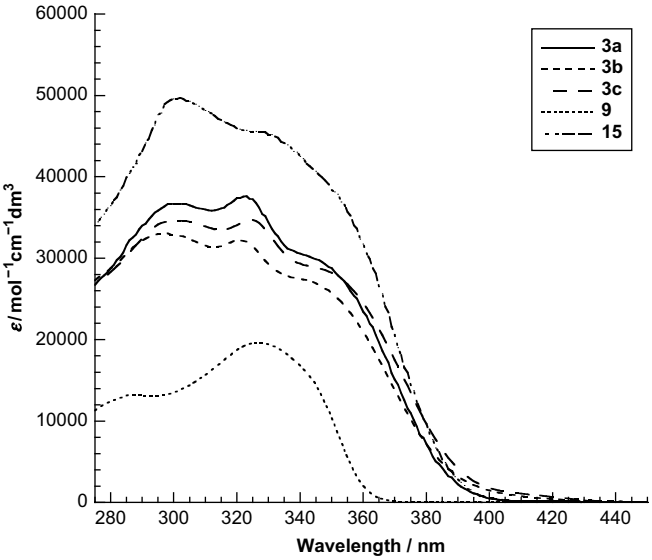


Figure 3. UV–vis spectra of **3a**–**c**, **9**, and **15** in CH_2Cl_2.

π-conjugation through the central phenylene moiety. Compound **14** with biphenyl moiety shows largest red shift and ε value, among the three trimethylsilyl-substituted derivatives. However, the difference in λ_{max} value between **14** and **2** is relatively small, indicating that extension of the π-system in **14** is not so good because coplanarity of the biphenyl moiety is not very good.

Figure 2 shows UV–vis spectra of phenylethynyl derivatives **7a**,**b**, **10**, **11**, and **16** in DMSO. Bathochromic shifts were observed in the order of **7b**>**7a**>**10**>**11**. The shape of the spectrum of **7b** in DMSO is significantly different from that in CH_2Cl_2 (Fig. 1), probably because red shifts of $\pi \rightarrow \pi^*$ transition occurred in more polar DMSO solvent. Similar to the cases of trimethylsilyl-substituted derivatives, compound **7a** exhibits much larger molar absorption coefficients, compared to **10** and **11** and the spectrum of **16** does not show significant red shift, compared to those of **7a**.

Similar results were obtained in the case of the pyridyl derivatives. Figure 3 shows absorption spectra of **3a**–**c** in CH_2Cl_2, along with those of **9**, and **15**. The spectra of **3a**–**c** and **7b** (Fig. 1) are relatively similar. Among the three isomers, **3a** shows the largest molar absorption coefficient at the two peaks of ca. 300 and 320 nm, with the order **3a**>**3c**>**3b**. Compound **15** possessing a biphenyl spacer shows much larger ε value in this region. As expected, **15** do not show significant red shift, compared to **3**. In contrast, the spectra of **3a**–**c** show large bathochromic shifts compared to those of compounds **10** and **1** (Fig. 1). Again, this fact indicates existence of significant π-conjugation through the central phenylene moiety in **3**, i.e., the π-system of 1,4-bis[2-(arylethynyl)-3-thienyl]benzene spreads throughout the molecule.

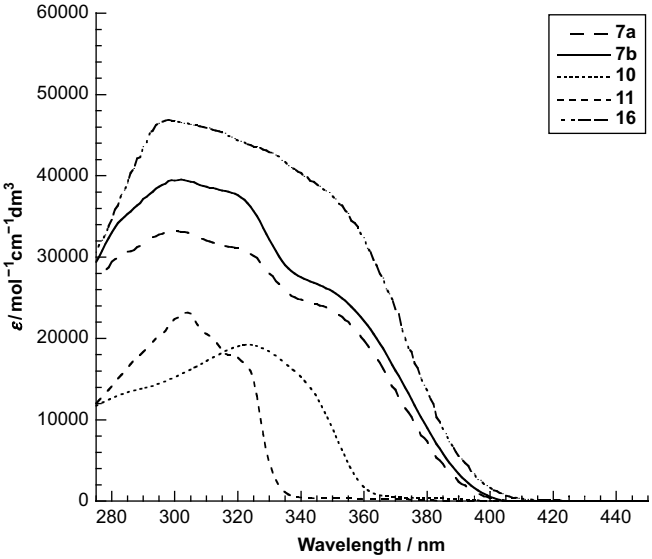
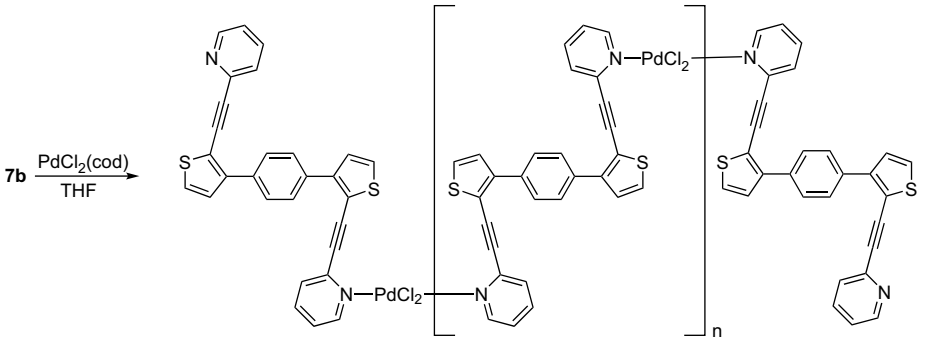


Figure 2. UV–vis spectra of **7a**,**b**, **10**, **11**, and **16** in dimethylsulfoxide.

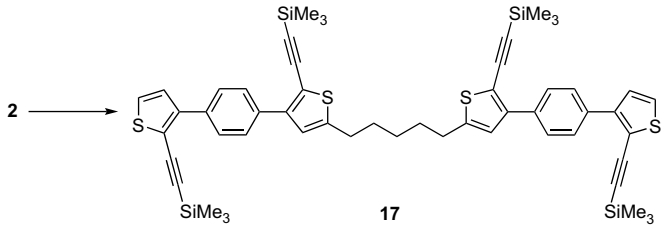
2.4. Some reactions of the ETB derivatives

When a clear yellow solution of **3a** and dichloro(1,5-cyclooctadiene)palladium(II) (1.1 equiv) in THF was kept at room temperature, pale yellow precipitate gradually formed. The precipitate was collected and washed with chloroform. Elemental analysis of the insoluble solid suggested formation of a dichloropalladium complex of **3a**. It is likely that the product is an intermolecular coordination polymer **3a**–$PdCl_2$, because there is not enough space for intramolecular chelation in the case of **3a**. Insolubility of the product may support coordination polymer structure. Elemental analysis data of the product approximately correspond to n=2 (Scheme 3), however, incorporation of other species in the solid is also feasible. It should be mentioned that a mixture of **7b** with dichloro(1,5-cyclooctadiene)palladium(II) did not show such a change under similar conditions, this fact may suggest that reaction at the triple bond of **3a** (or **7b**) did not occur under these conditions.

We then investigated connection of the ETB units (Scheme 4). Compound **2** was used as a representative of substituted ETB units, taking the solubility into account: to a solution of **2** in THF was added butyllithium and the resulting red solution was reacted with 1,5-diiodopentane to give **17** in 74% yield. The conversion methods described here, combined with those reported previously, are expected to become fundamental tools for construction of ETB-linked system, which may lead to artificial enzymes or metalloprotein-inspired molecules. Although there are problems in solubility and compatibility of metalation in some particular cases, further investigation on synthetic routes and strategy will conquer the problem.



Scheme 3.



Scheme 4.

3. Conclusion

In conclusion, we have prepared various bis[2-(arylethynyl or heteroarylethynyl)-3-thienyl]arene derivatives. Fundamental synthetic methods for ETB derivatives were studied, including connection of the ETB spacers, which may lead to construction of peptide-inspired architecture. Extension of π-system through the central benzene ring was suggested by UV–vis spectra and connection of the units was demonstrated in the case of the ETB derivatives. Further investigations on structure–property (such as redox properties and fluorescence) relationships are now in progress.

4. Experimental

4.1. General

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 JNM-GSX400. UV–vis spectra were measured on a Hitachi U-3210 spectrometer. 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. Gel permeation chromatography was carried out using Bio-Beads® S-X3 (Bio-Rad Laboratories, Inc., 200–400 mesh). In some cross-coupling experiments, silica-based palladium scavenger thiol (Silicycle, Nacalai Tesque Inc.) was used in the work-up process.

4.2. 1,4-Bis[2-{2-(2-pyridylethynyl)}-3-thienyl]benzene (3a)

A mixture of **6** (480 mg, 0.972 mmol), 2-ethynylpyridine (264.8 mg, 2.57 mmol), dichlorobis(triphenylphosphine)palladium(II) (96.9 mg, 0.138 mmol), copper(I) iodide (13.7 mg, 0.0719 mmol), and diisopropylamine (1 mL) in THF (15 mL) was stirred at 50 °C for 12 h. To the resulting mixture were added chloroform 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 5:1 to 0:1) to give 392.2 mg (0.571 mmol, 59% yield) of crude **3a**. The crude product was recrystallized from $CHCl_3$–hexane to give 232.8 mg (0.339 mmol, 35% yield) of **3a**. Pale yellow scales, mp 206–208 °C (decomp.); R_f=0.56 (SiO_2–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.23 (2H, m, pyridyl), 7.30 (2H, J=5.2 Hz, thienyl), 7.40 (2H, d, J=5.2 Hz, thienyl), 7.44 (2H, d, J=8.0 Hz, pyridyl), 7.61 (2H, ddd, J=15.6, 8.0, and 2.0 Hz, pyridyl), 7.95 (4H, s, phenyl), and 8.60 (2H, d, J=4.4 Hz, pyridyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ=83.6 (C≡C), 94.3 (C≡C), 117.2 (2-thienyl), 122.7, 127.1, 127.9, 128.0, 128.2, 134.6, 136.2, 143.2, 145.7, and 150.0; UV (CH_2Cl_2) 243 (log ε 4.45), 256 (4.46), 302 (4.56), 323 (4.58), and 342 nm (sh, 4.48); IR (KBr) 2201 (C≡C), 1580, 1561, 1539, 1505, 1466, 1439, 1426, 1404, 1368, 1302, 1281, 1246, 1152, 1113, 1088, 1048, 988, 872, 843, 830, 776, 750, 737, 631, 594, 534, and 504 cm^{-1}. Found: m/z 467.0644. Calcd for $C_{28}H_{16}N_2NaS_2$: M^++Na, 467.0647. Found: C, 74.34; H, 3.88, N, 6.23%. Calcd for $C_{28}H_{16}N_2S_2\cdot(H_2O)_{1/2}$: C, 74.14; H, 3.78; N, 6.18%.

4.3. 1,4-Bis[2-(2-phenylethynyl)-3-thienyl]benzene (7a)

A mixture of **6** (1.08 g, 2.19 mmol), ethynylbenzene (560 mg, 5.48 mmol), dichlorobis(triphenylphosphine)palladium(II) (220 mg, 0.313 mmol), copper(I) iodide (31.3 mg, 0.164 mmol), and diisopropylamine (2.4 mL) in THF (30 mL) was stirred at 50 °C for 24 h. After removal of an insoluble material by filtration, chloroform and water were added to the filtrate. 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 (hexane–$CHCl_3$ 50: 1) to give 700 mg (1.58 mmol, 72% yield) of crude **7a**. The crude product was dissolved in toluene (15 mL) and silica-based palladium scavenger thiol (40 mg) was added. The resulting mixture was stirred for 30 min, filtered, and the filtrate was concentrated under reduced pressure to give **7a** (200 mg, 0.452 mmol, 21% yield). Pale yellow powder, mp 194–196 °C; R_f=0.40 (SiO_2–CCl_4); ^{1}H NMR (400 MHz, DMSO-d_6) δ=7.34–7.41 (6H, m), 7.50–7.52 (6H, m), 7.74 (2H, m), and 8.03 (4H, s, phenyl); UV (DMSO) 283 (sh, log ε 4.48), 301 (4.52), 322 (sh, 4.49), and 349 nm (sh, 4.37); IR (KBr) 2191 (C≡C), 1593, 1503, 1487, 1487, 1433, 1300, 1067, 911, 870, 849, 822, 756, 737, 689, 652, 579, 529, and 502 cm^{-1}. Found: m/z 465.0740. Calcd for $C_{30}H_{18}NaS_2$: M^++Na, 465.0742. Found: C, 79.59; H, 4.25%. Calcd for $C_{30}H_{18}S_2\cdot(H_2O)_{1/2}$: C, 79.79; H, 4.24%. ^{13}C NMR spectrum was not measured because of the poor solubility.

4.4. 1,4-Bis[2-{2-(4-butylphenyl)ethynyl}-3-thienyl]-benzene (7b)

A mixture of **6** (1.6641 g, 3.37 mmol), 1-butyl-4-ethynylbenzene (1.1121 g, 7.03 mmol), dichlorobis(triphenylphosphine)palladium(II)

(354 mg, 0.504 mmol), copper(I) iodide (45 mg, 0.24 mmol), and diisopropylamine (5 mL) in THF (70 mL) was stirred at 50 °C for 40 h. Chloroform (ca. 200 mL) was added to the reaction mixture and an insoluble material was removed by filtration. 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 (hexane–$CHCl_3$ 1:0 to 2:1) to give 1.0677 g (1.92 mmol, 57% yield) of **7b**. Pale yellow powder, mp 109–111 °C; R_f=0.49 (SiO_2–CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.92 (6H, t, J=7.4 Hz, Me), 1.34 (4H, td, J=7.6, 7.4 Hz, CH_2Me), 1.58 (4H, quin, J=7.7 Hz, CH_2), 2.60 (4H, t, J=7.7 Hz), 7.10 (4H, d, J=8.2 Hz, 3′- and 5′-phenyl), 7.28 (2H, d, J=5.4 Hz, 4-thienyl), 7.31 (2H, d, J=5.4 Hz, 5-thienyl), 7.39 (4H, d, J=8.2 Hz, 2′- and 6′-phenyl), and 7.95 (4H, s, 2-, 3-, 5-, and 6-phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ=13.9 (CH_3), 22.3 (CH_2), 33.4 (CH_2), 35.6 (CH_2), 82.7 (C≡C), 95.7 (C≡C), 118.5 (2-thienyl), 120.1 (1′-phenyl), 126.3 (4-thienyl), 127.8 (5-thienyl), 127.9 (phenyl), 128.5 (phenyl), 131.2 (2′- and 3′-phenyl), 134.6 (1- and 4-phenyl), 143.5 (3-thienyl or 4′-phenyl), and 143.8 (3-thienyl or 4′-phenyl); UV (CH_2Cl_2) 241 (log ε 4.56), 283 (4.59), 296 (4.59), 319 (4.59), and 339 nm (sh, 4.51); UV (DMSO) 283 (sh, log ε 4.54), 301 (4.60), 322 (sh, 4.57), and 350 nm (sh, 4.41); IR (KBr) 2195 (C≡C), 1605, 1526, 1505, 1493, 1410, 1375, 1298, 1201, 1115, 1090, 1019, 866, 841, 727, 720, 644, 563, 529, and 504 cm^{-1}. Found: m/z 577.1993. Calcd for $C_{38}H_{34}NaS_2$: M^++Na, 577.1994.

4.5. 1,4-Bis[2-{2-(4-hexylphenyl)ethynyl}-3-thienyl]-benzene (7c)

A mixture of **6** (268.9 mg, 0.544 mmol), 1-ethynyl-4-hexylbenzene (289.6 mg, 1.55 mmol), dichlorobis(triphenylphosphine)-palladium(II) (56.0 mg, 0.080 mmol), copper(I) iodide (8.5 mg, 0.045 mmol), and diisopropylamine (0.6 mL) in THF (8 mL) was stirred at 50 °C for 24 h. Chloroform (ca. 20 mL) was added to the reaction mixture and an insoluble material was removed by filtration. 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 (hexane–CCl_4 1:0 to 0:1) to give 191.7 mg (0.314 mmol, 58% yield) of **7c**. Pale yellow solid, mp 86–88 °C; R_f=0.53 (SiO_2–CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (6H, t, J=6.7 Hz, Me), 1.29 (12H, m, CH_2), 1.59 (4H, m, CH_2), 2.59 (4H, t, J=7.7 Hz), 7.10 (4H, d, J=8.2 Hz, 3′- and 5′-phenyl), 7.28 (2H, d, J=5.3 Hz, 4-thienyl), 7.31 (2H, d, J=5.3 Hz, 5-thienyl), 7.39 (4H, d, J=8.2 Hz, 2′- and 6′-phenyl), and 7.95 (4H, s, 2-, 3-, 5-, and 6-phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ=14.1 (CH_3), 22.6 (CH_2), 28.9 (CH_2), 31.2 (CH_2), 31.7 (CH_2), 35.9 (CH_2), 82.7 (C≡C), 95.7 (C≡C), 118.4 (2-thienyl), 120.1 (1′-phenyl), 126.3 (4-thienyl), 127.8 (5-thienyl), 127.9 (phenyl), 128.5 (phenyl), 131.2 (2′- and 3′-phenyl), 134.5 (1- and 4-phenyl), 143.5 (3-thienyl or 4′-phenyl), and 143.8 (3-thienyl or 4′-phenyl); UV (CH_2Cl_2) 282 (log ε 4.43), 297 (4.44), 318 (4.44), and 342 nm (sh, 4.34); IR (KBr) 1526, 1505, 1458, 866, 841, 820, 722, 716, 644, 562, 538, 521, and 504 cm^{-1}. Found: m/z 633.2618. Calcd for $C_{42}H_{42}NaS_2$: M^++Na, 633.2620.

4.6. 3-Phenyl-2-[2-(trimethylsilyl)ethynyl]thiophene (8)

A mixture of 2-iodo-3-phenylthiophene[12] (307.1 mg, 1.073 mmol), ethynyltrimethylsilane (0.20 mL, 1.4 mmol), dichlorobis(triphenylphosphine)palladium(II) (33.4 mg, 0.048 mmol), copper(I) iodide (2.8 mg, 0.015 mmol), and diisopropylamine (1.5 mL) in THF (16 mL) was stirred at 50 °C for 48 h. Chloroform (ca. 100 mL) and water (ca. 100 mL) were added to the reaction mixture, the organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was treated with a silica-gel column chromatography (hexane) to give 149.6 mg (0.583 mmol, 54% yield) of **8**. Colorless oil; R_f=0.58 (SiO_2–CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.23 (9H, s, $SiMe_3$), 7.19 (1H, d, J=5.2 Hz, thienyl), 7.24 (1H, d, J=5.2 Hz, thienyl), 7.33 (1H, m, p-phenyl), 7.41 (2H, m, m-phenyl), and 7.81 (2H, m, o-phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ=−0.28 ($SiMe_3$), 98.2 (C≡C), 101.3 (C≡C), 117.9 (2-thienyl), 126.4, 127.6, 127.7, 127.9 (o-phenyl), 128.3 (m-phenyl), 135.1 (*ipso*-phenyl), and 145.4 (3-thienyl); UV (CH_2Cl_2) 292 nm (log ε 4.22); IR (neat) 2143 (C≡C), 1489, 1250, 1094, 876, 857, 843, 758, 722, 695, and 639 cm^{-1}; MS (70 eV) m/z (rel intensity) 256 (M^+, 79) and 241 (M^+−Me, 100). Found: m/z 256.0738. Calcd for $C_{15}H_{16}SSi$: M^+, 256.0737.

4.7. 3-Phenyl-2-[2-(2-pyridyl)ethynyl]thiophene (9)

A mixture of 2-iodo-3-phenylthiophene (170.5 mg, 0.596 mmol), 2-ethynylpyridine (0.080 mL, 0.792 mmol), dichlorobis(triphenylphosphine)palladium(II) (21.7 mg, 0.0309 mmol), copper(I) iodide (2.1 mg, 0.011 mmol), and diisopropylamine (1 mL) in THF (10 mL) was stirred at 50 °C for 24 h. Chloroform and water were added to the reaction mixture, the organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was treated with a silica-gel column chromatography ($CHCl_3$–EtOAc 1:0 to 25:1), silica-based palladium scavenger thiol (100 mg) and CCl_4 (10 mL) was added to crude **9**, and the mixture was stirred for 5 min. After removal of the scavenger by filtration, the solvent was removed under reduced pressure to give 58.4 mg (0.223 mmol, 37% yield) of **9**. Pale yellow oil; R_f=0.65 (SiO_2–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.21 (1H, ddd, J=7.6, 4.9, and 1.1 Hz, 5-pyridyl), 7.23 (1H, d, J=5.3 Hz, 4-thienyl), 7.35 (1H, d, J=5.3 Hz, 5-thienyl), 7.36 (1H, m, p-phenyl), 7.40 (1H, ddd, J=7.8, 1.1, and 0.9 Hz, 3-pyridyl), 7.45 (2H, m, m-phenyl), 7.64 (1H, ddd, J=7.8, 7.6, and 1.7 Hz, 4-pyridyl), 7.83 (2H, m, o-phenyl), and 8.60 (1H, ddd, J=4.9, 1.7, and 0.9 Hz, 6-pyridyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=83.3 (C≡C), 94.1 (C≡C), 117.0 (2-thienyl), 122.7 (5-pyridyl), 127.0 (3-pyridyl), 127.8 (p-phenyl), 128.0 (4-thienyl, o-phenyl), 128.5 (m-phenyl), 135.1 (*ipso*-phenyl), 136.0 (4-pyridyl), 143.3 (2-pyridyl), 146.1 (3-thienyl), and 150.1 (6-pyridyl); UV (CH_2Cl_2) 287 (log ε 4.12) and 326 nm (4.29); IR (neat) 2201 (C≡C), 1582, 1561, 1489, 1464, 1449, 1431, 1412, 1298, 1283, 1248, 1150, 1140, 988, 876, 776, 725, 696, 660, and 579 cm^{-1}. Found: m/z 262.0683. Calcd for $C_{17}H_{12}NS$: M^++H, 262.0685.

4.8. 3-Phenyl-2-(2-phenylethynyl)thiophene (10)

A mixture of 2-iodo-3-phenylthiophene (201.6 mg, 0.705 mmol), ethynylbenzene (0.1 mL, 0.91 mmol), dichlorobis-(triphenylphosphine)palladium(II) (24.9 mg, 0.0355 mmol), copper(I) iodide (1.4 mg, 0.0074 mmol), and diisopropylamine (1 mL) in THF (10 mL) was stirred at 50 °C for 36 h. Chloroform and water were added to the reaction mixture, the organic phase was washed with brine, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was treated with a silica-gel column chromatography using CCl_4 as an eluent. A silica-based palladium scavenger thiol (100 mg) was added to the collected fraction of **10** and the mixture was stirred for 10 min. After removal of the scavenger by filtration, the solvent was removed under reduced pressure to give 124.3 mg (0.477 mmol, 68% yield) of **10**. Pale yellow oil; R_f=0.49 (SiO_2–CCl_4); ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.21 (1H, d, J=5.3 Hz, 4-thienyl), 7.28 (1H, d, J=5.3 Hz, 5-thienyl), 7.3–7.4 (4H, m, p-, p'- and m'-phenyl), 7.4–7.5 (4H, m- and o'-phenyl), and 7.83 (2H, m, o-phenyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=83.3 (C≡C), 95.1 (C≡C), 118.1 (2-thienyl), 123.1 (*ipso*′-phenyl), 126.5 (5-thienyl), 127.6 (p-phenyl), 127.9 (o-phenyl), 128.0 (4-thienyl), 128.3 (p'-phenyl), 128.3 (m'-phenyl), 128.4 (m-phenyl), 131.3 (o'-phenyl), 135.3 (*ipso*-phenyl), and 144.7 (3-thienyl); UV (DMSO) 283 (sh, log ε 4.12) and 323 nm (4.28); UV (CH_2Cl_2) 247 (log ε 4.31), 280 (sh, 4.09),

and 321 nm (4.29); IR (neat) 2199 (C≡C), 1599, 1485, 1449, 1443, 1296, 1084, 1071, 914, 876, 768, 754, 723, 689, 656, and 565 cm^{-1}. Found: *m*/*z* 283.0552. Calcd for $C_{18}H_{12}NaS$: M^++Na, 283.0552.

4.9. 4,4′-Di(3-thienyl)biphenyl (12)

A mixture of 4,4′-diiodobiphenyl (1.23 g, 3.03 mmol), 3-thiopheneboronic acid (1.0 g, 7.81 mmol), tetrakis(triphenylphosphine)palladium (234 mg, 0.202 mmol), K_2CO_3 (4.10 g), toluene (15 mL), THF (10 mL), and water (5 mL) was heated at 85 °C for 24 h. Precipitates was collected by filtration and washed with chloroform to give **12** (900 mg, 2.83 mmol) in 93% yield. This compound was almost insoluble in common solvents and used in the succeeding reaction without recrystallization. Compound **12**. Colorless powder, mp>300 °C; IR (KBr) 1530, 1491, 1206, 866, 831, 777, and 635 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 318 (M^+; 100). Found: C, 69.84; H, 4.30%. Calcd for $C_{20}H_{14}S_2\cdot(H_2O)_{3/2}$: C, 69.53; H, 4.96%.

4.10. 4,4′-Bis(2-iodo-3-thienyl)biphenyl (13)

A suspension of **12** (100 mg, 0.314 mmol), *N*-iodosuccinimide (38.5 mg, 0.171 mmol, 0.54 molar ratio), and acetic acid (2 mL) in chloroform (5 mL) was stirred at 50 °C for 6 h. The insoluble starting material was removed by filtration and the filtrate 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–$CHCl_3$ 50:1) to give 20 mg (0.035 mmol, 41% yield based on *N*-iodosuccinimide) of **13** and 77.4 mg (77% recovery) of **12**. Compound **13**. Colorless powder, mp 180–184.5 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.02 (2H, dd, *J*=5.6 Hz, 4-thienyl), 7.52 (2H, d, *J*=5.6 Hz, 5-thienyl), 7.62 (4H, d, *J*=7.8 Hz, phenyl), and 7.72 (4H, d, *J*=7.8 Hz, phenyl); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ=73.1 (2-thienyl), 127.0 (biphenyl), 129.0 (5-thienyl), 129.2 (biphenyl), 131.2 (4-thienyl), 135.7 (*ipso*-biphenyl), 139.8 (*ipso*-biphenyl), and 146.2 (3-thienyl); UV (CH_2Cl_2) 258 (log ε 4.43) and 298 nm (4.56); IR (KBr) 1526, 1491, 1406, 1347, 1312, 1242, 1003, 953, 866, 831, 816, 779, 729, 714, 679, 652, 629, 519, and 469 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 570 (M^+, 100). Found: *m*/*z* 569.8471. Calcd for $C_{20}H_{12}I_2S_2$: M^+, 569.8464.

4.11. 4,4′-Bis[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]-biphenyl (14)

A mixture of **13** (crude, 364.6 mg, ca. 0.64 mmol), ethynyltrimethylsilane (226 μL, 1.6 mmol), dichlorobis(triphenylphosphine)palladium(II) (61.8 mg, 0.088 mmol), copper(I) iodide (8.9 mg, 0.047 mmol), and diisopropylamine (0.6 mL) in THF (9 mL) was stirred at 50 °C for 17 h. After removal of an insoluble material by filtration, chloroform and water were added to the filtrate. 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), and gel permeation column chromatography (Bio-Beads® S-X3 using CH_2Cl_2 as eluent) to give 46.0 mg (0.090 mmol, 14% yield) of **14**. Colorless scales, mp 214–216 °C; R_f=0.49 (SiO_2–CCl_4); ^{1}H NMR (600 MHz, $CDCl_3$) δ=0.26 (18H, s, $SiMe_3$), 7.24 (2H, d, *J*=5.1 Hz, 5-thienyl), 7.27 (2H, d, *J*=5.1 Hz, 4-thienyl), 7.69 (4H, AA′BB′, 2-, 2′-, 6-, 6′-phenyl), and 7.92 (4H, AA′BB′, 3-, 3′-, 5-, 5′-phenyl); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ=−0.23 ($SiMe_3$), 98.3 (TmsC≡*C*), 101.8 (Tms*C*≡C), 118.0 (2-thienyl), 126.5 (5-thienyl), 126.9 (2-, 2′-, 6-, 6′-phenyl), 127.6 (4-thienyl), 128.3 (3-, 3′-, 5-, 5′-phenyl), 134.3 (4-, 4′-phenyl), 139.8 (1-, 1′-phenyl), and 144.7 (3-thienyl); UV (CH_2Cl_2) 271 (log ε 4.51), 293 (4.52), 302 (4.52), and 329 nm (4.56); IR (KBr) 2143 (C≡C),1491, 1250, 1092, 847, 828, 758, 733, and 712 cm^{-1}. Found: *m*/*z* 533.1220. Calcd for $C_{30}H_{30}NaS_2Si_2$: M^++Na, 533.1220.

4.12. 4,4′-Bis[2-{2-(2-pyridyl)ethynyl}-3-thienyl]biphenyl (15)

A mixture of **13** (crude, 221 mg, ca. 0.39 mmol), 2-ethynylpyridine (151 mg, 1.46 mmol), dichlorobis(triphenylphosphine)-palladium(II) (49 mg, 0.698 mmol), copper(I) iodide (7.6 mg, 0.040 mmol), and diisopropylamine (0.6 mL) in THF (8 mL) was stirred at 50 °C for 24 h. To the resulting mixture were added chloroform and water. The organic phase 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–EtOAc 3:1), gel permeation chromatography (Bio-Beads® S-X3 using CH_2Cl_2 as eluent), and silica-based palladium scavenger thiol. The product was recrystallized from $CHCl_3$–EtOH to give 126 mg (0.242 mmol, 38% yield based on **12**) of **15**. Yellow scales, mp 273–275 °C; R_f=0.59 (SiO_2–EtOAc); ^{1}H NMR (400 MHz, CD_2Cl_2) δ=7.28–7.32 (2H, m, pyridyl), 7.35 (2H, d, *J*=5.2 Hz, thienyl), 7.47 (2H, d, *J*=5.2 Hz, thienyl), 7.51 (2H, d, *J*=8.0 Hz, pyridyl), 7.75 (2H, m, pyridyl), 7.82 (4H, m, phenyl), 7.99 (4H, m, phenyl), and 8.61 (2H, m, pyridyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ=83.7 (C≡C), 94.3 (C≡C), 117.1 (2-thienyl), 122.8 (arom), 127.1 (arom), 127.2 (arom), 127.9 (arom), 128.0 (arom), 128.5 (arom), 134.3 (arom), 136.3 (arom), 140.0 (arom), 143.2 (arom), 145.7 (arom), and 150.0 (arom); UV (CH_2Cl_2) 302 (log ε 4.70), 336 (sh, 4.65), and 349 nm (4.60); IR (KBr) 2201 (C≡C), 1582, 1561, 1493, 1466, 1420, 1298, 1283, 1244, 1150, 1003, 988, 874, 826, 776, 754, 745, 631, 579, and 502 cm^{-1}. Found: *m*/*z* 543.0957. Calcd for $C_{34}H_{20}N_2NaS_2$: M^++Na, 543.0960. Found: C, 77.07; H, 4.03; N, 5.31%. Calcd for $C_{34}H_{20}N_2S_2\cdot(H_2O)_{1/2}$: C, 77.10; H, 4.00, N, 5.29%.

4.13. 4,4′-Bis[2-(2-phenylethynyl)-3-thienyl]biphenyl (16)

A mixture of **13** (crude, 352 mg, ca. 0.62 mmol), ethynylbenzene (0.19 mL, 1.70 mmol), dichlorobis(triphenylphosphine)palladium(II) (49 mg, 0.095 mmol), copper(I) iodide (9.4 mg, 0.049 mmol), and diisopropylamine (0.8 mL) in THF (10 mL) was stirred at 50 °C for 24 h. To the resulting mixture were added chloroform and water. The organic phase was dried over $MgSO_4$, treated with silica-based palladium scavenger thiol, and the solvent was removed under reduced pressure. The residue was treated with a silica-gel column chromatography (hexane to hexane–CCl_4 10:1) and the product was recrystallized from hexane–$CHCl_3$ to give 103 mg (0.199 mmol) of **16** (20% yield based on **12**). Compound **16**. Yellow powder, mp 206–209 °C (decomp.); R_f=0.38 (SiO_2–CCl_4); ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.28 (2H, d, *J*=5.4 Hz, 4-thienyl), 7.33 (2H, d, *J*=5.4 Hz, 4-thienyl), 7.31–7.39 (6H, m, *m*- and *p*-Ph), 7.50 (4H, m, *o*-Ph), 7.75 (4H, d, *J*=8.4 Hz, phenyl), and 7.95 (4H, d, *J*=8.4 Hz, phenyl); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ=83.4 (C≡C), 95.4 (C≡C), 118.2 (2-thienyl), 123.1 (*ipso*-Ph), 126.6 (5-thienyl), 127.0 (biphenyl), 127.9 (4-thienyl), 128.4 (biphenyl+*m*- and *p*-Ph), 131.3 (*o*-Ph), 134.5 (*ipso*-biphenyl), 139.8 (*ipso*-biphenyl), and 144.2 (3-thienyl); UV (DMSO) 296 (log ε 4.67); UV (CH_2Cl_2) 293 (log ε 4.69) and 317 nm (sh, 4.64); IR (KBr) 2204 (C≡C), 1597, 1572, 1524, 1497, 1487, 1443, 1431, 1402, 1375, 1298, 1082, 1069, 1026, 1003, 909, 872, 824, 754, 735, 714, 687, 525, and 450 cm^{-1}. Found: *m*/*z* 541.1057. Calcd for $C_{36}H_{22}NaS_2$: M^++Na, 541.1055.

4.14. Reaction of 3a with dichloro(1,5-cyclo-octadiene)palladium(II)

Compound **3a** (27.5 mg, 0.0619 mmol) and dichloro(1,5-cyclo-octadiene)palladium(II) (18.9 mg, 0.0662 mmol) was solved in 15 mL of THF. The resulting clear yellow solution was kept at room temperature for 75 h and pale yellow precipitates formed

gradually. The precipitates were collected by filtration and washed with chloroform to give 26.7 mg (ca. 70% yield) of product. This product was hardly soluble in common solvent. Yellow solid; IR (KBr): 2197 (C≡C), 1593, 1563, 1478, 1426, 1246, 1159, 874, 853, 826, 774, and 737 cm^{-1}. Found: C, 57.23; H, 3.27; Cl, 8.90, N, 4.74, S, 10.94%. Calcd for $C_{28}H_{16}N_2S_2\cdot(Cl_2Pd)_{0.75}(H_2O)_{0.25}$: C, 57.78; H, 2.86, Cl, 9.14, N, 4.81, S, 11.02%.

4.15. Compound 17

To a solution of **2** (200 mg, 0.46 mmol) in THF (20 mL) was added 0.30 mL (0.48 mmol) of butyllithium (1.61 M solution in hexane) at −78 °C. The resulting mixture was stirred at −78 °C for 5 min and allowed to warm. This solution was transferred to a cooled solution (−78 °C) of 1,5-diiodopentane [30 μL (0.23 mmol)] in THF (5 mL). The reaction mixture was stirred at −78 °C for 5 min, allowed to warm to room temperature, and stirred at 50 °C for 4 h. To the resulting mixture were added chloroform and water. The organic phase was washed with brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Silica-gel column chromatography (hexane–$CHCl_3$ 3:1) followed by gel permeation column chromatography (Bio-Beads® S-X3 using CH_2Cl_2 as eluent) afforded 160 mg (0.17 mmol, 74% yield) of **17**. Colorless solid, mp 31–34 °C; R_f=0.15 (SiO_2–hexane); ^1H NMR (400 MHz, $CDCl_3$) δ=0.25 (18H, s, $SiMe_3$), 0.34 (18H, s, $SiMe_3$), 1.58 (6H, br, CH_2), 2.55 (4H, br, thienyl-CH_2), 7.19–7.31 (6H, m, thienyl), 7.79–7.81 (4H, m, Ph), and 7.86–7.88 (4H, m, phenyl); UV (CH_2Cl_2) 263 (log ε 4.79), 288 (4.75), and 322 nm (4.58); IR (KBr) 2141 (C≡C), 1539, 1491, 1406, 1350, 1250, 1177, 1115, 1090, 999, 839, 758, 723, 698, 652, 630, and 534 cm^{-1}. Found: *m*/*z* 959.2554. Calcd for $C_{53}H_{60}NaS_4Si_4$: M^++Na, 959.2547.

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