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Chemistry of bis(2-ethynyl-3-thienyl)arene and related systems. Part 6: preparation of 1,4-bis(2-ethynyl-3-thienyl)benzene derivatives containing fluorine atoms at the 2,3- or 2,5-positions of the benzene ring

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Chemistry of bis(2-ethynyl-3-thienyl)arene and related systems. Part 6: preparation of 1,4-bis(2-ethynyl-3-thienyl)benzene derivatives containing fluorine atoms at the 2,3- or 2,5-positions of the benzene ring

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

Fluorine-substituted 1,4-bis(2-ethynyl-3-thienyl)benzene derivatives were prepared, utilizing Suzuki–Miyaura and Sonogashira cross coupling reactions. Their UV spectra were compared with some related compounds.

Keywords: oligoarene; heterocycles; artificial molecular architecture; artificial enzyme; fluorobenzene

1. Introduction

Artificial large molecular systems, such as oligothiophenes, polythiophenes, and polymer complexes, have attracted much interest in the fields of physical organic chemistry, materials science, and synthetic organic chemistry (*1–4*). We previously applied the 2,3-thienylene moiety to the construction of oligoarenes and reported the development of the peptide-inspired 1,4-bis (2-ethynyl-3-thienyl)benzene spacer (Chart 1, abbreviated to the ETB spacer) (*5*), as well as 4,4′-bis(2-ethynyl-3-thienyl)biphenyl spacer (abbreviated to the ETAr spacer) (*6*), and the related compounds, such as **1**–**4** (*5*, *6*). The ETB spacer is a promising and easily tunable spacer of the three-ring system, which has a six-membered ring 1,4-phenylene moiety and a pair of five-membered ring 3-thienyl moieties at the both ends of the axis. Recent reports by Hamilton and co-workers (*7*) and Rebek and co-workers (*8*) also suggest the effectiveness of the 5-6-5 three-ring scaffold for peptide mimetics, although our ETB spacer is rather hydrophobic compared with Hamilton *et al.*'s imidazolyl-phenyl-thiazole system or Rebek *et al.*'s oxazolyl-pyridazyl-oxazole system, and the directions of the side chains are different. Our system (*5*, *6*, *9–11*) may have a chance to lead to peptide-inspired materials.

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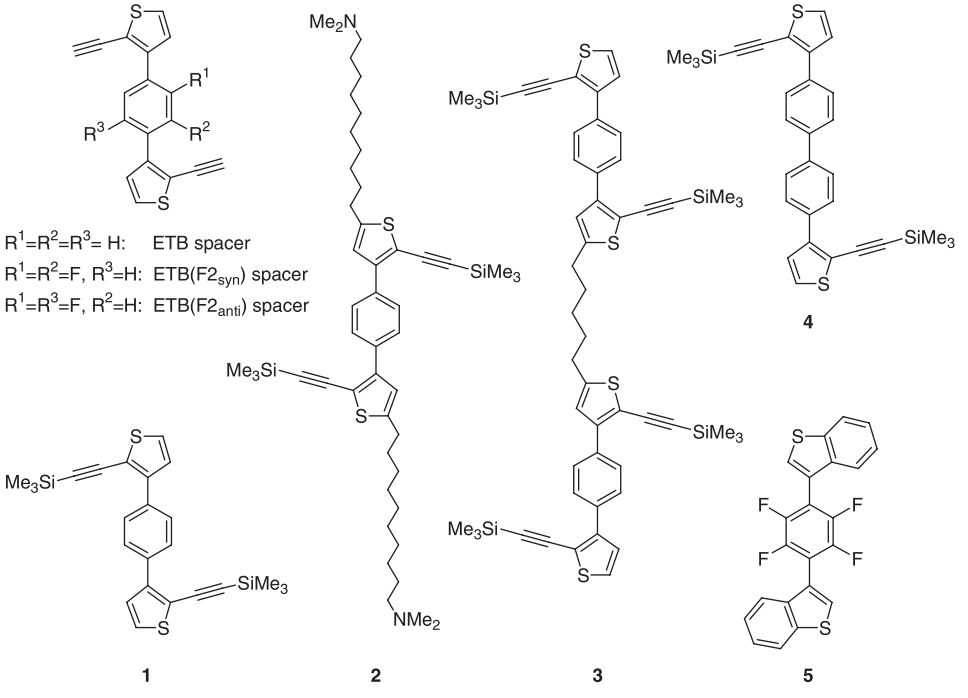


Chart 1.

In order to tune interactions between a bio-active small molecule and biopolymers, such as proteins and DNA, the introduction of fluorine substituents is often investigated, especially in the field of medicinal chemistry (*12*), because hydrogen and fluorine are similar in their size (van der Waals radius, Pauling's value: H, 1.2 Å; F, 1.35 Å) while their electronic properties are very different. The introduction of fluorine atoms to the 1,4-di(3-thienyl)benzene system is of interest also from the viewpoint of materials science, because it may lead to the development of intramolecular donor–acceptor system. In the case of the 1,4-di(*2-thienyl*)benzene system, many compounds containing fluorine atoms (on the central benzene ring) have been reported (*13*, *14*).

However, studies on the fluorine-substituted 1,4-di(*3-thienyl*)benzene derivatives are rare; 1,4-bis(3-benzo[*b*]thienyl)-2,3,5,6-tetrafluorobenzene (**5**) has been a single compound of this category reported so far, and the description of the properties was minimum (*15*). We report here preparations of 1,4-di(3-thienyl)benzene derivatives containing fluorine atoms at 2-,3- or 2-,5-positions of the benzene ring.

2. Results and discussion

We previously prepared 1,4-di(3-thienyl)benzene by the Suzuki–Miyaura coupling of 1,4-diiodobenzene and 3-thiopheneboronic acid (*5*). This time, we first tried to prepare 2,3-difluoro-1,4-di(3-thienyl)benzene (**8**) by the cross coupling reaction of 1-bromo-2,3-difluoro-4-iodobenzene with 3-thiopheneboronic acid; however, attempts to prepare the bromodifluoroiodobenzene, by a reaction of 1-bromo-2,3-difluorobenzene with lithium diisopropylamide (LDA) and 1,2-diiodoethane, suffered from low yield and difficulties in purification. When the crude product 1-bromo-2,3-difluoro-4-iodobenzene was reacted with

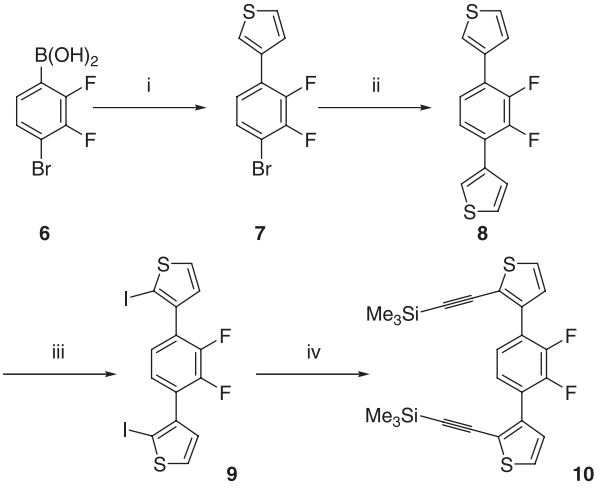
3-thiopheneboronic acid (ca. 2.5 equiv.) at 85 °C for 16 h, in the presence of $Pd(PPh_3)_4$, K_3PO_4, 1,4-dioxane, and water, the yield of **8** was ca. 15%.

We then tried to prepare **8** starting from a commercially available 4-bromo-2, 3-difluorobenzeneboronic acid (**6**) (Scheme 1): when **6** was reacted with 1.2 equiv. of 3-iodothiophene at 85 °C for 60 h in the presence of $Pd(PPh_3)_4$, K_2CO_3, toluene, tetrahydrofuran (THF), and water, the yield of **7** was only 22%. In this case, the reaction was slow and a considerable amount of 3-iodothiophene was recovered. When **6** was reacted with an excess amount of 3-iodothiophene (2 equiv.), using $PdCl_2$(dppf) and K_2CO_3 in 1,4-dioxane and water at 95 °C for 22 h, the yield of **7** was improved to 45%. It is noteworthy that 1-bromo-4-(3-thienyl)benzene derivatives such as **7** can be used to prepare unsymmetrical ETB derivatives (*9*).

Compound **7** thus obtained was converted to **8**, by the Suzuki–Miyaura cross coupling reaction with 3-thiopheneboronic acid, in 66% yield after purification. Compound **8** was iodinated with *N*-iodosuccinimide (NIS) in a regioselective manner (*5*, *16*) to form **9**, and the Sonogashira coupling of **9** with ethynyltrimethylsilane afforded **10** (44% yield based on **8**).

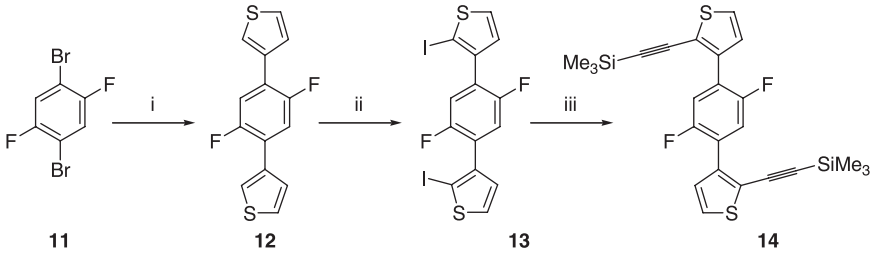
On the other hand, 1,4-difluoro-2,5-bis(2-ethynyl-3-thienyl)benzene derivative was prepared by a straightforward route starting from 1,4-dibromo-2,5-difluorobenzene (**11**) (Scheme 2): a cross coupling reaction of **11** with 3-thiopheneboronic acid gave 1,4-difluoro-2,5-di(3-thienyl)benzene (**12**) in 55% yield. Iodination of **12** with NIS followed by the Sonogashira coupling reaction afforded **14** via **13**.

Figure 1 shows UV spectra of **8**, **12**, and fluorine-free 1,4-di(3-thienyl)benzene (**15**) in dimethylsulfoxide. Compared with the absorptions of **12** and the parent **15**, considerable hypsochromic shift was observed in the case of **8** containing the 2,3-difluorobenzene ring, suggesting a larger HOMO–LUMO gap in **8**. Cyclic voltammetric measurement of **8** showed irreversible oxidation waves with Ep(ox) = 1.43 V (vs $Ag/AgNO_3$, 1 mM solution in benzonitrile, supporting electrolyte: Et_4NClO_4 (0.1 M), scan rate: 100 mVs^{-1}), while **15** exhibited an irreversible wave with Ep(ox) = 1.27 V. Compound **12** showed two irreversible oxidation waves with $Ep^1(ox) = 1.43$



Reagents and yield: i, 3-iodothiophene, $PdCl_2$(dppf), K_2CO_3, 1,4-dioxane, H_2O, 45%; ii, 3-thiopheneboronic acid, $Pd(PPh_3)_4$, PPh_3, K_3PO_4, 1,4-dioxane, H_2O, 66%; iii, NIS, AIBN, AcOH, $CHCl_3$; iv, ethynyltrimethylsilane, CuI, $PdCl_2(PPh_3)_2$, *i*-Pr_2NH, THF, 44% based on **8**.

Scheme 1.



Reagents and yield: i, 3-thiopheneboronic acid, $Pd(PPh_3)_4$, PPh_3, K_3PO_4, THF, H_2O, 55%; ii, NIS, AIBN, AcOH, $CHCl_3$, 39%; iii, ethynyltrimethylsilane, CuI, $PdCl_2(PPh_3)_2$, *i*-Pr_2NH, THF, 28%.

Scheme 2.

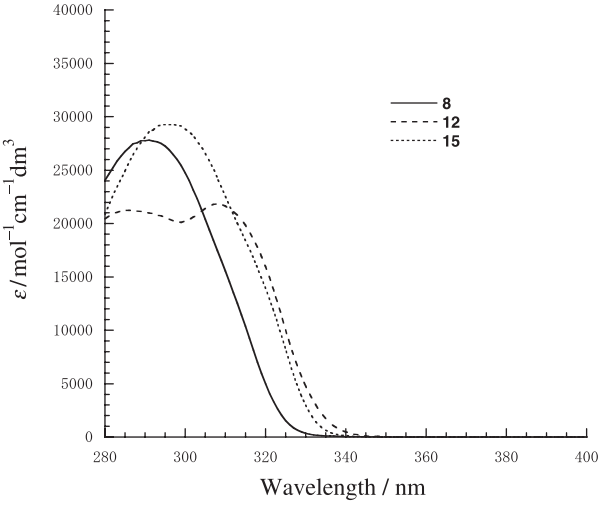


Figure 1. UV spectra of **8**, **12**, and 1,4-di(3-thienyl)benzene (**15**) in dimethylsulfoxide.

and $Ep^2(ox) = 1.69\,V$, under similar conditions. For compounds **8**, **12**, and **15**, no significant reduction wave was observed in the 0 to $-2.0\,V$ region.

UV spectra of **1**, **10**, and **14** in CH_2Cl_2 are shown in Figure 2. Compound **10**, possessing the ETB ($F2_{syn}$) spacer (Chart 1) showed blue shift compared with **1** and **14**. Probably, coplanarity of the three rings in the 2,3-difluoro-1,4-di(3-thienyl)benzene is not so good as those of 1,4-difluoro-2,5-di(3-thienyl)benzene and the fluorine-free 1,4-di(3-thienyl)benzene. It should be mentioned that the parent 1,4-di(3-thienyl)benzene **15** is soluble in dimethylsulfoxide but hardly soluble in CH_2Cl_2, while **8** and **12** show good solubility in both dimethylsulfoxide and CH_2Cl_2. This fact may support the above discussion on the coplanarity, because a large system with good coplanarity often causes π-stacking and becomes insoluble in common solvents. However, we suspend a conclusion until we have prepared and evaluated other fluorine-substituted congeners, such as 1,3-difluoro-2,5-di(3-thienyl)benzene or 1,2,4,5-tetrafluoro-3,6-di(3-thienyl)benzene.

In summary, we have prepared compounds containing novel fluorine-substituted spacers, ETB($F2_{syn}$) and ETB($F2_{anti}$). Good solubility was observed in the cases of ETB($F2_{syn}$) and ETB($F2_{anti}$) derivatives, which may allow construction of sophisticated oligomeric systems, as shown in Chart 2. Further investigation on the ETB(F) spacers and their derivatives are in progress.

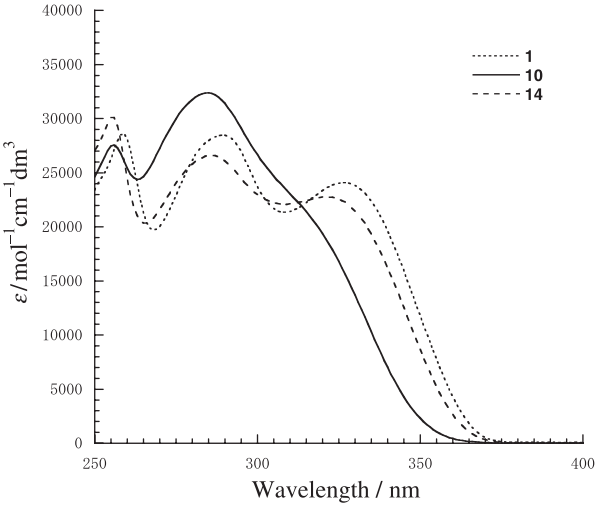
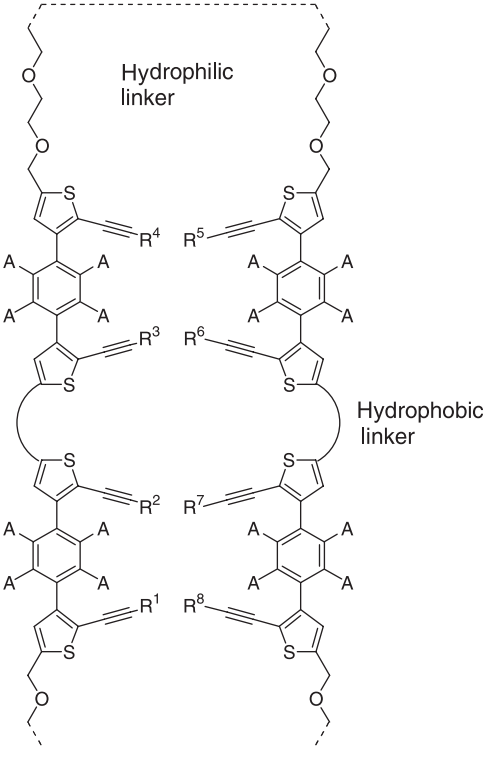


Figure 2. UV spectra of **1**, **10**, and **14** in dichloromethane.



Concept of peptide-inspired ETB materials

Chart 2.

3. 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. UV–visible 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-ion cyclotron resonance-mass spectra were measured on a Bruker APEX III spectrometer.

3.1. *1-Bromo-2,3-difluoro-4-(3-thienyl)benzene (7)*

A mixture of 3-iodothiophene (361.4 mg, 1.72 mmol), 4-bromo-2,3-difluorobenzeneboronic acid (**6**) (204.2 mg, 0.862 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (63.5 mg, 0.0868 mmol), K_2CO_3 (588.9 g, 4.26 mmol), 1,4-dioxane (15 ml), and water (5 ml) was heated at 95 °C for 22 h. After cooling to room temperature, chloroform (ca. 50 ml) and water (ca. 50 ml) were added to the reaction mixture, and 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 (hexane) to give 106.2 mg (0.386 mmol, 45% yield based on **6**) of **7**: Colorless oil; $R_f = 0.39$ (SiO_2–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.64$ (1H, m, 2-thienyl), 7.43 (1H, dd, $J = 5.0$ hz and 2.9 hz, 5-thienyl), 7.39 (1H, br d, $J = 5.0$ hz, 4-thienyl), 7.34 (1H, m, phenyl), and 7.23 (1H, m, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 148.8$ (dd, $^1J_{FC} = 248.2$ hz, $^2J_{FC} = 15.2$ hz, phenyl), 148.3 (dd, $^1J_{FC} = 254.0$ hz, $^2J_{FC} = 14.3$ hz, phenyl), 133.9 (s, 3-thienyl), 127.7 (d, $J_{FC} = 4.3$ hz, thienyl), 127.1 (d, $J_{FC} = 3.4$ hz, thienyl), 126.1 (s, thienyl), 125.1 (d, $^2J_{FC} = 10.4$ hz, 4-phenyl), 124.4 (d, $^3J_{FC} = 3.4$ hz, 6-phenyl), 124.1 (dd, $^3J_{FC} =^4 J_{FC} = 3.7$ hz, 5-phenyl), and 108.3 (d, $^2J_{FC} = 18.1$ hz, 1-phenyl); IR (neat) 3112, 1532, 1480, 1457, 1362, 1231, 953, 882, 851, and 782 cm^{-1}. MS (70 eV) m/z (rel. intensity) 276 (M^++2; 100), 274 (M^+; 97), 231 (M^+–SCH+2; 6), 229 (M^+–SCH; 6), and 151 (M^+–SCH–Br+1; 18). Calcd for $C_{10}H_5BrF_2S$: M^+ 273.9258. Found: m/z 273.9263.

3.2. *2,3-Difluoro-1,4-di(3-thienyl)benzene (8)*

A mixture of **7** (94.2 mg, 0.342 mmol), 3-thiopheneboronic acid (56.1 mg, 0.438 mmol), tetrakis(triphenylphosphine)palladium (17.0 mg, 0.0147 mmol), triphenylphosphine (26.0 mg, 0.0991 mmol), K_3PO_4 (469.8 mg, 2.21 mmol), 1,4-dioxane (20 ml), and water (6 ml) was heated at 80 °C for 5 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. Silica-gel column chromatographic separation (chloroform as an eluent) of the residue gave 94.4 mg (0.339 mmol, 99% yield) of crude product, which was recrystallized from hexane to afford 63.1 mg (0.227 mmol, 66% yield) of **8**: Colorless scales, mp 133–134 °C; $R_f = 0.68$ (SiO_2–$CHCl_3$), 0.24 (SiO_2–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.68$ (2H, m, 2-thienyl), 7.46 (2H, br d, $J = 5.1$ hz, 4-thienyl), 7.43 (2H, dd, $J = 5.1$ hz and 2.9 hz, 5-thienyl), and 7.4–7.3 (2H, m, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 148.5$ (dd, $^1J_{FC} = 251.4$ hz, $^2J_{FC} = 15.8$ hz, 2- and 3-phenyl), 134.4 (s, 3-thienyl), 127.1 (s, 5-thienyl), 125.7 (s, 4-thienyl), 123.9 (dd, $^3J_{FC} =^4 J_{FC} = 3.3$ hz, 2-thienyl), 123.8 (dd, $^2J_{FC} = 6.7$ hz, $^3J_{FC} = 3.9$ hz, 1- and 4-phenyl), and 123.3 (dd, $^3J_{FC} =^4 J_{FC} = 3.8$ hz, 5- and 6-phenyl); UV (CH_2Cl_2) 287 nm (log ε4.53); UV (DMSO) 291 nm (log ε 4.44); IR (KBr) 3115, 1453, 1358, 1221, 1103, 961, 851, 785, 660, and 577 cm^{-1}. MS (70 eV) m/z (rel. intensity) 278 (M^+; 100), 233 (M^+–SCH; 8), and 139 ($M^+/2$; 5). Found: m/z 278.0033. Calcd

for $C_{14}H_8F_2S_2$: M^+ 278.0035. Found: C, 60.27; H, 3.20%. Calcd for $C_{14}H_8F_2S_2$: C, 60.41; H, 2.90%.

3.3. *2,3-Difluoro-1,4-bis[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]benzene (10)*

A mixture of **8** (24.2 mg, 0.0869 mmol), NIS (47.9 mg, 0.213 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN, 3.5 mg, 0.0213 mmol), acetic acid (1 ml), and chloroform (10 ml) was stirred at 50 °C for 3 h. After cooling to room temperature, chloroform (ca. 20 ml) and water (ca. 20 ml) were added to the reaction mixture. The organic phase was washed with saturated aqueous $NaHCO_3$ and then saturated aqueous $Na_2S_2O_3$ solution. The organic phase was separated, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with a short silica-gel column (eluent = CCl_4) to give 39.2 mg (ca. 0.074 mmol) of crude **9** (ca. 85% yield). A mixture of crude **9** (38.4 mg, ca. 0.072 mmol), ethynyltrimethylsilane (0.04 ml, 0.283 mmol), dichlorobis(triphenylphosphine)palladium(II) (7.1 mg, 0.010 mmol), copper(I) iodide (3.3 mg, 0.017 mmol), and *N*,*N*-diisopropylamine (1.6 ml) in THF (5 ml) was stirred at 50 °C for 8 h. After cooling to room temperature, chloroform (ca. 30 ml) and water (ca. 30 ml) were added to the reaction mixture. The organic phase was separated, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated on a silica-gel column (eluent = hexane to hexane-EtOAc 3:1) to give 18.1 mg (0.0384 mmol, ca. 53% yield) of **10** (44% yield based on **8**): Colorless prisms, mp 114–116 °C; R_f = 0.71 (SiO_2–CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (2H, m, 4- and 5-phenyl), 7.30 (2H, d, J = 5.3 hz, thienyl), 7.25 (2H, br d, J = 5.3 hz, thienyl), and 0.22 (18H, s, $SiMe_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 148.1 (dd, $^1J_{FC}$ = 252.5 hz and $^4J_{FC}$ = 15.8 hz, 2- and 3-phenyl), 138.0 (s, 3-thienyl), 128.7 (m, thienyl), 126.2 (s, thienyl), 124.4 (dd, $^3J_{FC}$ = $^4J_{FC}$ = 3.4 hz, 5- and 6-phenyl), 124.1 (dd, $^2J_{FC}$ = 7.2 hz and $^3J_{FC}$ = 4.4 hz, 1- and 4-phenyl), 120.8 (s, 2-thienyl), 102.3 (s, C≡C), 97.1 (s, C≡C), and –0.4 (s, $SiMe_3$); UV (CH_2Cl_2) 256 (log ε 4.44) and 285 nm (4.51); IR (KBr) 2961, 2143 (C≡C), 1489, 1458, 1408, 1250, 1215, 1175, 1142, 1082, 994, 853, 762, and 733 cm^{-1}. FT-ICR-MS Found: m/z 493.0717. Calcd for $C_{24}H_{24}F_2NaS_2Si_2$: M^++Na, 493.0718.

3.4. *1,4-Difluoro-2,5-di(3-thienyl)benzene (12)*

A mixture of 1,4-dibromo-2,5-difluorobenzene (**11**, 1.9937 g, 7.33 mmol), 3-thiopheneboronic acid (2.3512 g, 18.374 mmol), tetrakis(triphenylphosphine)palladium (89.4 mg, 0.0774 mmol), triphenylphosphine (311.4 mg, 1.19 mmol), K_3PO_4 (8.5841 g, 40.4 mmol), THF (100 ml), and water (50 ml) was heated at 75 °C for 3 days. After cooling to room temperature, chloroform (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 rinsed with a small amount of chloroform. The unsolved product **12** was collected by filtration (1.1298 g, 4.06 mmol, 55% yield). **12**: Colorless powder, mp 138–139 °C; R_f = 0.21 (SiO_2–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (2H, pseudo t, J = 1.4 hz, 2-thienyl), 7.45 − 7.41 (4H, m, 4- and 5-thienyl), and 7.35 (2H, dd, $^3J_{FH}$ = $^4J_{FH}$ = 9.1 hz, 3- and 6-phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 155.6 (dd, $^1J_{FC}$ = 244.2 hz and $^4J_{FC}$ = 3.5 hz, 1- and 4-phenyl), 134.4 (s, 3-thienyl), 127.0 (s, 5-thienyl), 125.8 (s, 4-thienyl), 124.1 (dd, $^4J_{FC}$ = $^5J_{FC}$ = 3.9 hz, 2-thienyl), 123.0 (dd, $^2J_{FC}$ = $^3J_{FC}$ = 12.0 hz, 2- and 5-phenyl), and 116.1 (m, 3- and 6-phenyl); UV (CH_2Cl_2) 281 (log ε 4.42) and 306 nm (4.40); UV (DMSO) 286 (log ε 4.33) and 308 nm (4.34); IR (KBr) 3112, 1584, 1539, 1503, 1433, 1356, 1287, 1252, 1215, 1171, 1096, 1048, 905, 882, 830, 797, 760, 695, 600, and 473 cm^{-1}. MS (70 eV) m/z (rel. intensity) 278 (M^+; 100), 233 (M^+−SCH; 11), and 139 ($M^+/2$; 6). Found: m/z 278.0033. Calcd for $C_{14}H_8F_2S_2$: M^+, 278.0035. Found: C, 60.39; H, 3.06%. Calcd for $C_{14}H_8F_2S_2$: C, 60.41; H, 2.90%.

3.5. *1,4-Difluoro-2,5-bis(2-iodo-3-thienyl)benzene (13)*

A mixture of **12** (1.0140 g, 3.643 mmol), NIS (1.7724 g, 7.878 mmol), AIBN (66.1 mg, 0.403 mmol), acetic acid (15 ml), and $CHCl_3$ (30 ml) was stirred at 50 °C for 3 h. After cooling to room temperature, chloroform (ca. 30 ml) and water (ca. 40 ml) were added to the reaction mixture. The organic phase was washed with saturated aqueous $NaHCO_3$ and then with saturated aqueous $Na_2S_2O_3$ solution. The organic phase was separated, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with a silica-gel column (eluent = CCl_4) to give a crude product, which was rinsed with 20 ml of hexane, and the hexane-soluble by-products were removed by filtration to give 750.4 mg (1.416 mmol, 39% yield) of **13**: Colorless powder, mp 164–166 °C; $R_f = 0.18$ (SiO_2–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.54$ (2H, d, $J = 5.4$ hz, 5-thienyl), 7.25 (2H, dd, $^3J_{FH} = {}^4J_{FH} = 7.9$ hz, phenyl), and 7.02 (2H, d, $J = 5.4$ hz, 4-thienyl); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) $\delta = 154.8$ (dd, $^1J_{FC} = 244.8$ hz and $^4J_{FC} = 3.7$ hz, 1- and 4-phenyl), 139.7 (d, $^3J_{FC} = 4.2$ hz, 3-thienyl), 131.2 (s, 5-thienyl), 129.3 (s, 4-thienyl), 125.3 (dd, $^2J_{FC} = 14.6$ hz, $^3J_{FC} = 11.7$ hz, 2- and 5-phenyl), 118.5 (dd, $^2J_{FC} = 11.0$ hz, $^3J_{FC} = 6.6$ hz, 3- and 6-phenyl), and 76.1 (s, 2-thienyl); IR (KBr) 3106, 1545, 1483, 1428, 1385, 1331, 1225, 1196, 1173, 1113, 1076, 963, 889, 880, 872, 820, 772, 727, 685, 656, 604, 478, and 459 cm^{-1}. MS (70 eV) m/z (rel. intensity) 530 (M^+; 100), 404 (M^+−I+1; 8), 359 (M^+−I–SCH+1; 4), and 276 (M^+−2I; 9). Found: m/z 529.7968. Calcd for $C_{14}H_6F_2I_2S_2$: M^+, 529.7968. Found: C, 31.71; H, 1.37%. Calcd for $C_{14}H_6F_2I_2S_2$: C, 31.72; H, 1.14%.

3.6. *1,4-Difluoro-2,5-bis[2-{2-(trimethylsilyl)ethynyl}-3-thienyl]benzene (14)*

A mixture of **13** (503.1 mg, 0.949 mmol), ethynyltrimethylsilane (0.30 ml, 2.123 mmol), dichlorobis(triphenylphosphine)palladium(II) (94.9 mg, 0.135 mmol), copper(I) iodide (26.1 mg, 0.137 mmol), and diisopropylamine (20 ml) in THF (40 ml) was stirred at 50 °C for 3 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, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated on a silica-gel column (eluent = CCl_4) to give a crude product, which was rinsed with 5 ml of hexane, and the hexane-soluble by-products were removed by filtration to give 123.5 mg (0.262 mmol, 28% yield) of **14**: Colorless powder, mp 138–140 °C; $R_f = 0.59$ (SiO_2–CCl_4); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.80$ (2H, dd, $^3J_{FH} = {}^4J_{FH} = 8.9$ hz, 3- and 6-phenyl), 7.30 (2H, br d, $J = 5.3$ hz, thienyl), 7.28 (2H, d, $J = 5.3$ hz, thienyl), and 0.24 (18H, s, $SiMe_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 154.8$ (dd, $^1J_{FC} = 245.0$ hz and $^4J_{FC} = 3.6$ hz, 1- and 4-phenyl), 137.8 (s, 3-thienyl), 128.7 (t, $J_{FC} = 3.6$ hz, thienyl), 126.0 (s, thienyl), 123.2 (dd, $^2J_{FC} = 13.9$ hz, $^3J_{FC} = 11.1$ hz, 2- and 5-phenyl), 120.6 (s, 2-thienyl), 117.7–117.3 (m, 3- and 6-phenyl), 102.9 (s, C≡C), 97.1 (s, C≡C), and −0.5 (s, $SiMe_3$); UV (CH_2Cl_2) 255 (log ε 4.47), 285 (4.42), and 321 nm (4.35); IR (KBr) 3125, 2957, 2899, 2139 (C≡C), 1539, 1487, 1437, 1404, 1347, 1285, 1252, 1240, 1183, 1161, 1103, 1090, 887, 882, 860, 845, 783, 754, 741, 689, 656, 613, 519, and 471 cm^{-1}. MS (70 eV) m/z (rel. intensity) 470 (M^+; 100), 367 (M^+–Me_3Si–2Me; 16), and 73 (Me_3Si^+; 21). Found: m/z 470.0821. Calcd for $C_{24}H_{24}F_2S_2Si_2$: M^+, 470.0826. Found: C, 60.85; H, 5.09%. Calcd for $C_{24}H_{24}F_2S_2Si_2$: C, 61.23; H, 5.14%.

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