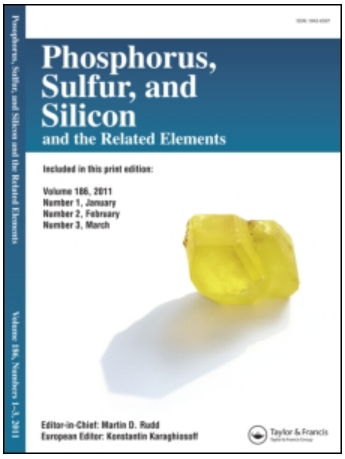

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Facile, Convenient Synthesis of Highly Pure ω-Ferrocenylalkanethiols as Probes for Self-Assembled Monolayer (SAM) on Gold Surface

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FACILE, CONVENIENT SYNTHESIS OF HIGHLY PURE ω-FERROCENYLALKANETHIOLS AS PROBES FOR SELF-ASSEMBLED MONOLAYER (SAM) ON GOLD SURFACE

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High purity synthesis of ω-ferrocenylalkanethiols ($Fc(CH_2)_n$-SH, n=6, 8, 11) was developed for their use in self-assembled monolayers on gold surface. The method employs a separation and purification of isothiuronium salt **6** to improve the purity of final products **7**. The use of hazardous mercury in the Clemmensen reduction of acylferrocene **4** to alkylferrocenes **5** is avoided by an alternative LAH / $AlCl_3$ reduction.

Keywords: probe for self-assembled monolayer (SAM); ω-ferrocenylalkanethiols; high purity synthesis; isothiuronium salt; LAH/$AlCl_3$ reduction of acylferrocene

INTRODUCTION

Long chain alkanethiols form stable self-assembled monolayer (SAM) on a gold surface.[1)] The alkanethiols containing a terminal ferrocenyl group (Fc) with various alkyl chain lengths are used extensively for the probes in the physicochemical or electrochemical studies on the SAMs on gold surfaces.[2)] The synthetic method for Fc-thiols is outlined in many examples,

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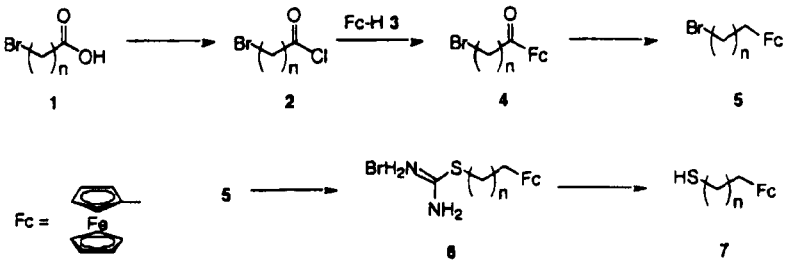
but there are few detailed descriptions on the synthesis. The employed method appears straightforward;[3] Friedel- Crafts acylation of ferrocene with ω-bromoalkanoyl chlorides, Clemmensen reduction of the ketone to Fc-alkyl bromide, and its reaction with thiourea to the thiol derivatives. We developed the new synthetic method as convenient as possible, while the purity of the final products is assured by isolating and purifying the crystalline intermediate isothiuronium salts. The use of hazardous mercury in the Clemmensen reduction is also avoided by the use of an alternative reduction with $LiAlH_4/AlCl_3$.[4]

RESULTS AND DISCUSSION

The new synthetic method is shown in SCHEME 1.



SCHEME 1

ω-Bromoalkanoic acid **1** was heated with excess thionyl chloride to give the corresponding acid chloride **2** which was distilled briefly on a Kugelrohr apparatus. The Friedel-Crafts acylation of ferrocene **3** with the acid chloride was performed with $AlCl_3$ catalyst in dichloromethane at 0 °C to give a mixture of the desired ω-bromoalkanoylferrocene **4**, a small amount of the unreacted ferrocene **3**, and some unidentifiable by-products. The glc analysis showed that the by-products constitute up to 10 % of product. In the case of 11-bromoundecanoylferrocene **4c**, the product was purified by crystallization. In the other cases, a chromatographic separation of the ω-bromoalkanoylferrocene **4** might be recommended but is not convenient, since the following reduction of the mixture with $LAH/AlCl_3$ gave

only a mixture of the desired ω-bromoalkylferrocene **5** and the remaining ferrocene **3**. The by-products in the acylation mixture should be reduced to the desired ω-bromoalkylferrocene **5** during the reaction with $LAH/AlCl_3$. Therefore, (*E*)- and (*Z*)-isomers of the ferricenium enolate were assumed for such by-products.

The reduction of aromatic ketones to methylene compounds with $LAH/AlCl_3$ is applicable to those with electron-rich aromatic rings.[4] The electron-rich ferrocenyl ketones **4** meet the requirement and the reduction of **4** to **5** was effectively performed in ether at room temperature in good yield. This reduction needs no mercury as frequently used in the other syntheses.[3]

The intermediate products **4** and **5** were not isolated as described above, but their structures were confirmed by IR, ^1H and ^{13}C NMR spectra. ^{13}C NMR of **5** showed that no double acylation occurred during the Friedel-Crafts acylation of ferrocene **3**. This means that the $AlCl_3$ complex of the carbonyl group in **4** deactivates effectively the cyclopentadienyl ring on the other side.

The ω-bromoalkylferrocene **5** (containing a small amount of ferrocene **3**) was reacted with thiourea in refluxing methanol to give the corresponding isothiuronium bromide **6**. The isolation and purification are critical in this synthetic method to assure the high purity of the final product **7**. The mixture was chromatographed on silica gel. A small amount of ferrocene **3** eluted quickly with dichloromethane. Then the isothiuronium bromide **6** eluted with dichloromethane-methanol and was purified by crystallization from methanol by adding ether. The structure of **6** was confirmed by ^1H, ^{13}C NMR, and IR spectra. The isothiuronium salts were decomposed to the desired ω-ferrocenylalkanethiols with methanolic alkali under reflux. The products were purified by column chromatography to give analytically pure **7**. The yields of **6** and **7** were somewhat low as compared with the similar conversion employed recently for the synthesis of an ω-aminoalkanethiol.[5] The major reason may be the oxidation of the ferrocenyl group to the higher oxidation state, as suggested by the contamination of dark brown materials. This could be avoided by adding an appropriate reducing reagent to the reaction mixture; however, this problem was not resolved in this study.

EXPERIMENTAL

6-Bromohexanoyl Chloride 2a

A mixture of 6-bromohexanoic acid **1a** (10.03 g, 51.4 mmol) and thionyl chloride (26 mL, 0.35 mol) was stirred at 40 °C for 2 h under dry atmosphere, and heated to reflux for 1 h. The excess thionyl chloride was evaporated under reduced pressure and the residue was distilled by Kugelrohr to give **2a** (10.63 g, 96.8%) as colorless liquid, bp 110–130 °C/20 mm Hg.

6-Bromohexanoylferrocene 4a

A solution of 6-bromohexanoyl chloride **2a** (10.63 g, 49.8 mmol) and ferrocene **3** (10.18 g, 54.7 mmol) in dichloromethane (25 mL) was cooled over ice-water bath under argon, and then aluminum chloride (6.65 g, 49.9 mmol) was added to the solution carefully in small portions. The mixture was stirred at room temperature for 1 h, hydrolyzed by adding ice and water (300 mL) with cooling over ice-water bath, and extracted with dichloromethane (100 mL). The organic layer was filtered to remove trace insoluble material, and concentrated under reduced pressure to give a residue (19.12 g) which was used in the next step without further purification.

The glc analysis of the residue showed **4a** (82.3 %) (estimated yield 75.5 % based on **3** used), unreacted **3** (7.3 %), and several unidentifiable products, almost all of which could be reduced to **5a** in the next step. ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.48 (2 H, m), 1.68 (2 H, quint, J = 7.4 Hz), 1.86 (2 H, quint, J = 7.1 Hz), 2.66 (2 H, t, J = 7.3 Hz, CH_2COFe), 3.38 (2 H, t, J = 6.8 Hz, CH_2Br), 4.14 (5 H, s, Fc), 4.44 (2 H, t, J = 2.0 Hz, Fc), and 4.73 ppm (2 H, t, J = 1.8 Hz, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 23.56 (CH_2), 28.05 (CH_2), 32.65 (CH2), 33.72 (CH_2), 39.38 (CH_2), 69.28 (2 CH), 69.76 (5 CH), 72.20 (2 CH), 79.01 (C), and 204.26 ppm (CO).

6-Bromohexylferrocene 5a

A solution of crude **4a** (20.98 g, 57.8 mmol) in ether (40 mL) was added to a mixture of aluminum chloride (15.20 g, 114 mmol) and ether (70 mL) with ice-water cooling under argon, and the mixture was stirred for 0.5 h with cooling. Lithium aluminum hydride (3.29 g, 86.8 mmol) was added

to the mixture carefully with cooling and the mixture was stirred at room temperature for 1 h. The excess LAH was decomposed by adding ice and water (300 mL), and then the mixture was acidified with hydrochloric acid (110 mL), and extracted with dichloromethane (200 mL). The organic layer was filtered to remove insoluble material, and concentrated under reduced pressure to give a residue (20.79 g) which was used in the next step without further purification.

The glc analysis of the residue showed **5a** (93.1 %) (estimated yield 92 % from **3** used), unreacted **3** (6.3 %), and the sum of three unidentifiable by-products (0.6 %).

5a, dark brown oil; ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.29–1.56 (6 H, m), 1.86 (2 H, quint, J = 7.0 Hz), 2.32 (2 H, t, J = 7.6 Hz, CH_2Fc), 3.41 (2 H, t, J= 6.8 Hz, CH_2Br), 4.04 (4 H, broad s, Fc), and 4.09 ppm (5 H, s, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 28.04 (CH2), 28.68 (CH_2), 29.46 (CH_2), 30.94 (CH_2), 32.76 (CH_2), 34.00 (CH2), 67.06 (2 CH), 68.06 (2 CH), 68.48 (5 CH), and 89.24 ppm (C). IR (KBr) ν 3094 (w), 2934 (s), 2858 (m), 1106 (m), 1002 (m), 818 (m) and 484 cm^{-1} (m).

Isothiuronium bromide 6a

A mixture of crude **5a** (20.79 g, 59.6 mmol), thiourea (5.00 g, 65.7 mmol), and methanol (30 mL) was heated to reflux for 5 h under argon. The resulting solution was concentrated under reduced pressure and the residue was chromatographed on silica-gel column (Wako-gel C 200); dichloromethane eluted undesired ferrocene, and then dichloromethane – methanol (9:1) eluted the desired isothiuronium bromide **6a**, which was reprecipitated from methanol by adding ether.

6a (18.97 g, 44.6 mmol, 74 % from **3**), light brown powder, mp 108.0–110.0 °C (from MeOH-ether). ^{1}H NMR (CD_3OD, 270.2 MHz) δ 1.35–1.56 (6 H, m), 1.71 (2 H, quint, J = 7.5 Hz), 2.34 (2 H, t, J = 7.6 Hz, CH_2Fc), 3.11 (2 H, t, J = 7.3 Hz, CH_2Br), 4.05 (4 H, broad s, Fc), 4.10 (5 H, s, Fc), and 4.25 ppm (4 H, broad s, CD_3OH exchanged). ^{13}C NMR (CD_3OD, 67.9 MHz) δ 28.42 (CH_2), 28.54 (CH2), 29.06 (CH_2), 29.68 (CH_2), 31.12 (CH_2), 31.16 (CH_2), 67.30 (2 CH), 68.28 (2 CH), 68.68 (5 CH), 89.28 (C), and 171.74 ppm (C). IR (KBr) ν 3186 (m), 3084 (m), 2928 (m), 2858 (m), 1655 (s), 1437 (m), and 692 cm^{-1} (m).

6-Mercaptohexylferrocene 7a

A mixture of the isothiuronium bromide **6a** (10.0 g, 23.6 mmol), sodium hydroxide (2.74 g, 68.4 mmol), and methanol (15 mL) was refluxed under argon for 5 h. The mixture was cooled, diluted with water (100 mL), acidified with hydrochloric acid (10 mL), and extracted with dichloromethane (50 mL). The residue obtained was chromatographed on silica gel (Wako gel C-200, eluent hexane). The fast running fraction was collected and distilled by Kugelrohr to give **7a** as red crystal.

7a (4.56 g, 15.1 mmol, 64 % from **6a**), purity 99.5 % (by glc), mp 27.5–28.5 °C, bp 155–170 °C / 0.3 mm Hg. ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.25–1.66 (8 H, m), 1.33 (1 H, t, J = 7.9 Hz, SH), 2.31 (2 H, t, J = 7.8 Hz, CH_2Fc), 2.52 (2 H, q, J = 7.4 Hz, CH_2SH), 4.04 (4 H, broad s, Fc), and 4.08 ppm (5 H, s, Fc). ^{13}C NMR (CD_3OD, 67.9 MHz) δ 24.64 (CH_2), 28.22 (CH_2), 29.00 (CH_2), 29.50 (CH_2), 31.00 (CH_2), 33.98 (CH_2), 67.02 (2 CH), 68.04(2 CH), 68.44 (5 CH), and 89.28 ppm (C). IR (KBr) ν 2924 (s), 2854 (s), 2560 (m, SH), 1464 (m), 1104 (m), 1000 (m), 812 (m), and 485 (s) cm^{-1}. Found: C, 63.38; H, 7.30. Calcd. for $C_{16}H_{22}FeS$: C, 63.58; H, 7.34 %.

8-Bromooctanoyl Chloride 2b

A mixture of 8-bromooctanoic acid **1b** (5.05 g, 22.6 mmol) and thionyl chloride (14.5 g, 122 mmol) was heated to reflux for 5 h. The excess thionyl chloride was distilled off under reduced pressure and the residue was distilled by Kugelrohr to give **2b** (5.16 g, mmol, 94 %) as a pale yellow oil, bp 90–145 °C/20 mm Hg.

8-Bromooctanoylferrocene 4b

A solution of 8-bromooctanoyl chloride **2b** (5.16 g, 21.4 mmol) and ferrocene **3** (4.37 g, 23.5 mmol) in dichloromethane (15 mL) was cooled in an ice-water bath under argon, and then aluminum chloride (2.85 g, 21.4 mmol) was added to the solution carefully in small portions. The mixture was refluxed for 1 h, hydrolyzed by adding water (50 mL), and extracted with dichloromethane (50 mL). The organic layer was concentrated under reduced pressure to give a residue (8.04 g) which was used in the next step without further purification.

The glc analysis of the residue showed **4b** (89.0 %, estimated yield 78 % based on **3** used), unreacted **3** (3.3 %), and some unidentifiable products (7.7 %), almost all of which could be reduced to **5b** in the next step.

4b, dark red oil. ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.35–1.55 (6 H, m), 1.71 (2 H, m), 1.88 (2 H, quint, J = 7.2 Hz), 2.70 (2 H, t, J = 7.4 Hz, CH_2COFc), 3.42 (2 H, t, J = 6.9 Hz, CH_2Br), 4.20 (5 H, s, Fc), 4.49 (2 H, t, J = 1.8 Hz, Fc), and 4.78 ppm (2 H, t, J = 2.0 Hz, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 24.46 (CH_2), 28.04 (CH_2), 28.68 (CH_2), 29.32 (CH_2), 32.76 (CH_2), 34.00 (CH_2), 39.64 (CH_2), 69.32 (2 CH), 69.74 (5 CH), 72.14 (2 CH), 79.14 (C), and 204.58 ppm (CO). IR (KBr) ν 2934 (m), 2858 (m), 1669 (s), 1456 (m), 824 (m), and 482 cm^{-1} (m).

8-Bromooctylferrocene 5b

A solution of crude **4b** (8.04 g, 20.6 mmol) in ether (20 mL) was added to a mixture of aluminum chloride (5.01 g, 37.6 mmol) and ether (50 mL) with ice-water cooling under argon, and the mixture was stirred for 0.5 h with cooling. Lithium aluminum hydride (1.06 g, 27.9 mmol) was added to the mixture carefully with cooling and the mixture was stirred at room temperature for 1 h. The excess LAH was decomposed by adding water (50 mL), and then the mixture was acidified with hydrochloric acid (20 mL), and extracted with dichloromethane (50 mL). The organic layer was filtered and evaporated under reduced pressure to give a residue (6.72 g) which was used in the next step without further purification.

The glc analysis of the residue showed **5b** (97.7 %, estimated yield 74.1 % from **3** used), unreacted **3** (1.8 %), and the sum of by-products (0.5 %).

5b, dark red oil. 1H NMR ($CDCl_3$, 270.2 MHz) δ 1.31 (6 H, broad s), 1.35–1.54 (4 H, m), 1.85 (2 H, quint, J = 7.1 Hz), 2.31 (2 H, t, J = 7.6 Hz, CH_2Fc), 3.41 (2 H, t, J = 6.9 Hz, CH_2Br), 4.04 (2 H, broad s, Fc), 4.04 (2 H, broad s, Fc), and 4.09 ppm (5 H, s, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 28.14 (CH_2), 28.72 (CH_2), 29.30 (CH_2), 29.48 (CH_2), 29.56 (CH_2), 31.06 (CH_2), 32.80 (CH_2), 34.06 (CH_2), 66.98 (2 CH), 68.04 (2 CH), 68.44 (5 CH), and 89.45 ppm (C). IR (KBr) ν 3096 (m), 2930 (s), 2858 (s), 1464 (m), 1106 (m), 1002 (m), and 818 cm^{-1} (m).

Isothiuronium bromide 6b

A mixture of crude **5b** (6.72 g, 17.8 mmol), thiourea (1.46 g, 19.2 mmol), and methanol (10 mL) was heated to reflux for 5 h under argon. The solu-

tion was concentrated under reduced pressure and the residue was chromatographed on silica-gel column (Wako-gel C 200); dichloromethane eluted undesired ferrocene, and then dichloromethane – methanol (4:1) eluted the desired isothiuronium bromide **6b**, which was reprecipitated from methanol by adding ether.

6b (6.73 g, 14.8 mmol, 63 % from **3**), yellow crystals, mp 85.5–89.5 °C (from MeOH-ether). ^{1}H NMR (CD_3OD, 270.2 MHz) δ 1.34 (6 H, broad s), 1.41–1.56 (4 H, m), 1.72 (2 H, quint, J = 7.3 Hz), 2.32 (2 H, t, J = 7.6 Hz, CH_2Fe), 3.13 (2 H, t, J= 7.3 Hz, CH_2Br), 4.04 (2 H, broad s, Fc), 4.05 (2 H, broad s, Fc), and 4.10 ppm (5 H, s, Fc). ^{13}C NMR (CD_3OD, 67.9 MHz) δ 29.18 (CH_2), 29.29 (CH_2), 28.80 (CH_2), 30.10 (CH_2), 30.22 (CH_2), 30.36 (CH_2), 31.64 (CH_2), 31.96 (CH_2), 67.86 (2 CH), 68.90 (2 CH), 69.26 (5 CH), 90.28 (C), and 172.74 ppm (CO). IR (KBr) ν 3202 (m), 3080 (s), 2928 (m), 2856 (m), 1655 (s), 820 (m), and 669 cm^{-1} (m).

8-Mercaptooctylferrocene 7b

A mixture of isothiuronium bromide **6b** (6.73 g, 14.8 mmol), sodium hydroxide (1.08 g, 27 mmol), methanol (20 mL) was heated to reflux under argon for 5 h. The mixture was diluted with water, acidified with hydrochloric acid, and extracted with dichloromethane. The organic layer was concentrated to give a residue, which was chromatographed on Wako-gel C 200; hexane eluted the desired ferrocenyl thiol **7b**, which solidified in a refrigerator and was washed with small amount of methanol at 0 °C. Yield (2.82 g, 8.54 mmol, 58 % from **6b**), yellow solid, mp 38.0–38.5 °C. ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.22–1.53 (12 H, broad m), 1.32 (1 H, t, J = 7.8 Hz, SH), 1.60 (2 H, quint, J = 7.4 Hz), 2.30 (2 H, t, J = 7.8 Hz, CH_2Fe), 2.51 (2 H, q, J = 7.4 Hz, CH_2SH), 4.03 (2 H, broad s, Fc), 4.03 (2 H, broad s, Fc), and 4.08 ppm (5 H, s, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 24.62 (CH_2), 28.32 (CH_2), 29.00 (CH_2), 29.34 (CH_2), 29.52 (2 CH_2), 31.06 (CH_2), 34.00 (CH_2), 66.94 (2 CH), 68.00 (2 CH), 68.39 (5 CH), and 89.42 ppm (C). IR (KBr) ν 3084 (w), 2992 (s), 2850 (s), 2558 (m, SH), 1466 (m), 1104 (w), 998 (w), 810 (m), and 484 cm^{-1} (m). Found: C, 65.46; H, 7.92. Calcd. for $C_{18}H_{26}FeS$: C, 65.45; H, 7.93 %.

11-Bromoundecanoyl Chloride 2c

A mixture of 11-bromoundecanoic acid (11.20 g, 42.2 mmol) and thionyl chloride (12.49 g, 105 mmol) was stirred at 40°C for 2 h, and refluxed for 1 h. Kugelrohr distillation of the resultant solution gave the chloride **2c** (11.81 g, mmol, 98.6 %) as a pale yellow liquid.

11-Bromoundecanoylferrocene 4c

Aluminum chloride (6.18 g, 46.3 mmol) was added carefully to a solution of 11-bromoundecanoyl chloride **2c**(11.81 g, 41.6 mmol) and ferrocene **3** (8.60 g, 46.2 mmol) in dichloromethane (25 mL) with cooling over ice-water bath. The mixture was stirred at room temperature for 1 h, hydrolyzed by addition of ice and water (300 mL), and extracted with dichloromethane (100 mL). The organic layer was concentrated, and the residue was recrystallized from methanol to give **4c** as a brown powder.

4c (17.75 g, 41.0 mmol, 89 % from **3**), purity 94.8 % by glc, mp 57.0–58.0 °C (from MeOH). ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.25–1.50 (12 H, m), 1.63–1.76 (2 H, m), 1.86 (2 H, quint, J= 7.1 Hz), 2.69 (2 H, t, J = 7.4 Hz, CH2COFc), 3.41 (2 H, t, J = 6.9 Hz, CH_2Br), 4.20 (5 H, s, Fc), 4.49 (2 H, t, J = 2.0 Hz, Fc), and 4.78 ppm (2 H, t, J = 2.0 Hz, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 24.60 (CH_2), 28.14 (CH_2), 28.74 (CH2), 29.38 (2 CH_2), 29.46 (CH_2), 29.52 (CH_2), 32.82 (CH_2), 34.08 (CH_2), 39.73 (CH_2), 69.32 (2 CH), 69.72 (5 CH), 72.10 (2 CH), 79.18 (C), and 204.70 ppm (CO). IR (KBr) ν2920 (s), 2854 (m), 1661 (s), 1458 (m), 1257 (m), 826 (m), 499 (m), and 482 cm^{-1} (m).

11-Bromoundecylferrocene 5c

Aluminum chloride (10.75 g, 81 mmol) was added to a solution of 11-bromoundecanoylferrocene **4c** (17.75 g, 41.0 mmol) under argon in an ice-water bath, and lithium aluminum hydride (2.42 g, 64 mmol) was added to the mixture. The mixture was stirred at room temperature for 1 h, ice was added to decompose the excess LAH, and it was acidified with hydrochloric acid (100 mL), and extracted with dichloromethane to give a residue **5c**, which solidified upon standing.

5c (16.49 g, 39.3 mmol, 96 % from **4c**), brown solid, mp 38.0–41.5 °C, purity 98.9 % (by glc). ^{1}H NMR ($CDCl_3$, 270.2 MHz) δ 1.28 (12 H, broad

s), 1.28–1.55 (4 H, m), 1.85 (2 H, quint, $J = 7.1$ Hz), 2.31 (2 H, t, $J = 7.8$ Hz, CH_2Fc), 3.41 (2 H, t, $J = 6.8$ Hz, CH_2Br), 4.03 (2 H, d, $J = 1.3$ Hz, Fc), 4.05 (2 H, d, $J = 1.3$ Hz, Fc), and 4.09 ppm (5 H, s, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 28.16 (CH_2), 28.76 (CH_2), 29.42 (CH_2), 29.50 (2 CH_2), 29.56 (2 CH_2), 29.64 (CH_2), 31.10 (CH_2), 32.82 (CH_2), 34.06 (CH_2), 66.96 (2 CH), 68.04 (2 CH), 68.42 (5 CH), and 89.56 ppm (C). IR (KBr) ν 2932 (s), 2852 (s), 1468 (m), 818 (s), and 497 cm^{-1} (s).

Isothiuronium bromide 6c

A mixture of 11-bromoundecylferrocene **5c** (16.49 g, 39.3 mmol), thiourea (3.29 g, 43 mmol), and methanol (10 mL) was refluxed for 5 h under argon. The mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel column (Wako gel C-200); dichloromethane eluted the undesired products, and then dichloromethane-methanol (9:1) eluted **6c**, which was recrystallized from methanol-ether to give yellow crystals (14.94 g, 30.2 mmol, 77 % from **5c**).

6c, mp 128–128.5 °C (from MeOH-ether). 1H NMR (CD_3OD, 270.2 MHz) δ 1.31 (12 H, broad s), 1.41–1.56 (4 H, m), 1.71 (2 H, quint, $J = 7.3$ Hz), 2.32 (2 H, t, $J = 7.6$ Hz, CH_2Fc), 3.13 (2 H, t, $J = 7.3$ Hz, CH_2-isothiuronium), 4.03 (2 H, broad s, Fc), 4.04 (2 H, broad s, Fc), and 4.07 ppm (5 H, s, Fc). ^{13}C NMR (CD_3OD, 67.9 MHz) δ 29.22 (CH_2), 29.32 (CH_2), 29.84 (CH_2), 30.26 (CH_2), 30.35 (2 CH_2), 30.38 (3 CH_2), 31.68 (CH_2), 32.02 (CH_2), 67.80 (2 CH), 68.86 (2 CH), 69.20 (5 CH), 90.30 (C), and 172.70 ppm (CO). IR (KBr) ν3178 (s), 3076 (s), 2924 (s), 2852 (s), 1655 (s), 818 (m), 690 (m), and 487 cm^{-1} (m).

11-Mercaptoundecylferrocene 7c

A mixture of the isothiuronium bromide **6c** (13.60 g, 27.4 mmol), sodium hydroxide (2.21 g, 55.4 mmol), and methanol (40 mL) was heated to reflux under argon for 5 h. The mixture was diluted with water, acidified with hydrochloric acid at room temperature, and extracted with dichloromethane (50 mL) to give a residue which was chromatographed on silica gel (Wako gel C-200); hexane eluted **7c** as yellow crystals which were washed with a small amount of methanol at 0 °C. Yield (7.32 g, 19.7 mmol, 72 % from **6c**), mp 39.5–41.0 °C. 1H NMR ($CDCl_3$, 270.2 MHz) δ

1.27 (14 H, broad s), 1.32 (1 H, t, J= 7.8 Hz, SH), 1.48 (2 H, m), 1.60 (2 H, quint, J = 7.3 Hz), 2.30 (2 H, t, J= 7.8 Hz, CH_2Fc), 2.51 (2 H, q, J = 7.4 Hz, $C\underline{H}_2SH$), 4.03 (2 H, m, Fc), 4.04 (2 H, m, Fc), and 4.08 ppm (5 H, s, Fc). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 24.66 (CH_2), 28.38 (CH_2), 29.06 (CH_2), 29.50 (2 CH_2), 29.56 (3 CH_2), 29.64 (CH2), 31.10 (CH_2), 34.06 (CH_2), 66.96 (2 CH), 68.04 (2 CH), 68.42 (5 CH), and 89.56 ppm (C). IR (KBr) ν 2920 (s), 2852 (s), 2562 (w, SH), 1470 (m), 810 (m), and 480 cm^{-1} (m). Found: C, 67.80; H, 8.49. Calcd. for $C_{21}H_{32}FeS$: C, 67.73; H, 8.66 %.

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