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Syntheses of Polythia[*n*]ferrocenophanes and Polythia[*n.n*]-ferrocenophanes. Marocyclic Polysulfide Ligands Containing a Ferrocene Nucleus

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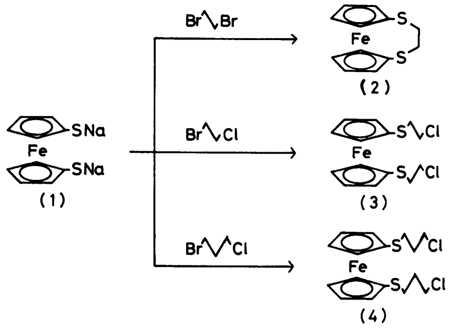
1,1′-Bis(2-chloroethylthio)ferrocene reacted with disodium 1,2-ethanedithiolate to give 1,4,7,10-tetrathia-[10]ferrocenophane and 1,4,7,10,22,25,28,31-octathia[10.10]ferrocenophane, along with unexpected 1,4,7-trithia-[7]ferrocenophane, 1,4,7,10,13-pentathia[13]ferrocenophane and 1,4,7,10,13,25,28,31,34-nonathia[10.13]ferrocenophane. The reaction of 1,1′-bis(2-chloroethylthio)ferrocene with disodium 1,3-propanedithiolate gave 1,4,-8,11-tetrathia[11]ferrocneophane. 1,1′-Bis(3-chloropropylthio)ferrocene reacted with disodium 1,2-ethanedithiolate and 1,3-propanedithiolate to afford 1,5,8,12-tetrathia[12]ferrocenophane and 1,5,8,12,24,27,31,34-octathia-[12.12]ferrocenophane, and 1,5,9,13-tetrathia[13]ferrocenophane, respectively. The structural features of the above polythia[*n*]ferrocenophanes are also discussed on the bases of their spectral data.

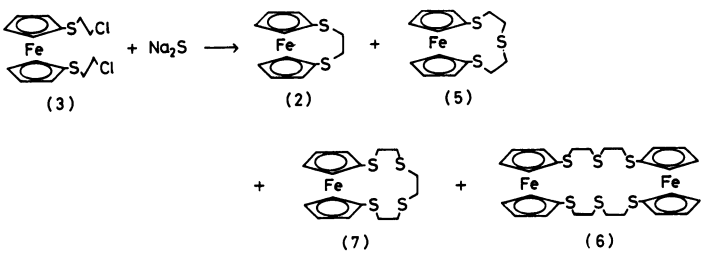
Various types of crown ethers have been prepared and their functionalities investigated.[1] The first thia-crown ether was synthesized in 1934[2] and thereafter some thia-macrocyclic compounds have been prepared[3–6] and shown to have a high affinity toward transition metal cations.[3,7–9] Especially, the complex with a copper atom has attracted much attention as a model of the blue copper protein,[8] nevertheless, the modified thia-crown ethers have scarcely been reported. Polythiaferrocenophanes, in which a ferrocene nucleus is incorporated in the framework of a thia-crown ether ring, is a new type of these modified thia-crown compounds. We now report on the preparation of several polythia[*n*]ferrocenophanes and polythia[*n.n*]-ferrocenophanes.[10]

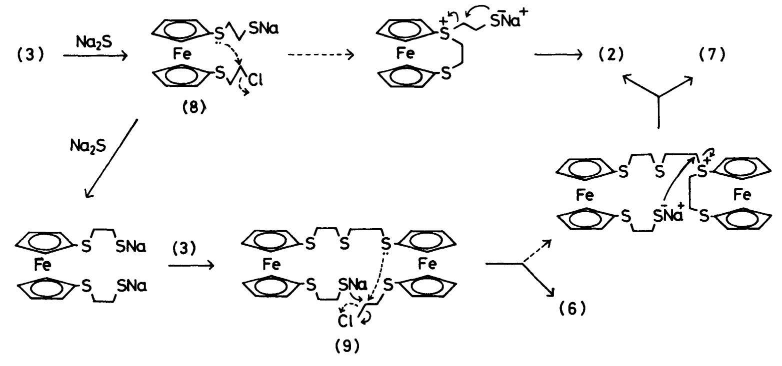
Disodium 1,1′-ferrocenedithiolate (**1**), which was prepared from 1,1′-ferrocenedithiol[11] and sodium hydroxide in ethanol, reacted with 1,2-dibromoethane in ethanol at room temperature to give 1,4-dithia[4]-ferrocenophane (**2**) as orange crystals in 37% yield. Although a polymeric compound was produced, no dimer of **2** was isolated. In the ^{1}H-NMR spectrum of **2**, the α- and β-protons of ferrocene rings appeared as two well-separated doublets at δ 4.41 and 4.19, suggesting the presence of a little tilt-deformation in the two cyclopentadienyl rings of the ferrocene nucleus.[12] The bridging methylene protons resonated downfield, δ 3.33; this would be explained by the fact that they are rigidly held in a deshielding zone between two cyclopentadienyl rings.[13]

Compound **1** reacted with 1-bromo-2-chloroethane in ethanol to give 1,1′-bis(2-chloroethylthio)ferrocene (**3**) as yellow crystals in 67% yield, along with a small amount of **2**. The ^{1}H-NMR spectrum of **3** showed the methylene protons as a A_2X_2 pattern at δ 2.86 (t, 4H, J=8.7 Hz) and 3.57 (t, 4H, J=8.7 Hz), supporting the assigned structure. Similarly, **1** reacted with 1-bromo-3-chloropropane to give 1,1′-bis(3-chloropropylthio)ferrocene (**4**) as an orange oil in 71% yield. The ^{1}H-NMR spectrum, which showed the methylene protons as two triplets at δ 2.71 (4H, J=6.5 Hz, CH_2S) and 3.61 (4H, J=6.5 Hz, CH_2Cl) and a pentuplet at δ 1.94 (4H, $CH_2C\underline{H_2}CH_2$) and the ring protons as a multiplet at δ 4.24, confirmed the proposed structure.

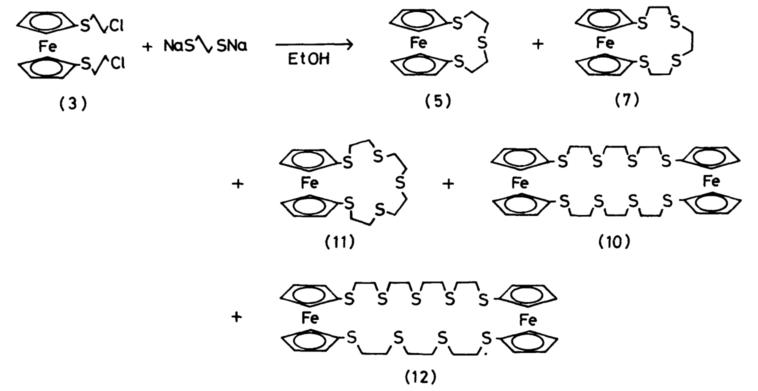
A solution of dichloride **3** in dry tetrahydrofuran (THF) was added all at once to a solution of sodium sulfide nonahydrate in ethanol and the resulting solution was refluxed for 10 h. After the usual work-up, the reaction mixture was chromatographed on silica gel to give a moderate yield (27.5%) of 1,4,7-trithia[7]-ferrocenophane (**5**) and a trace amount of the dimer, 1,4,7,19,22,25-hexathia[7.7]ferrocenophane (**6**), along with unexpected 1,4-dithia[4]ferrocenophane (**2**) (5.0%)





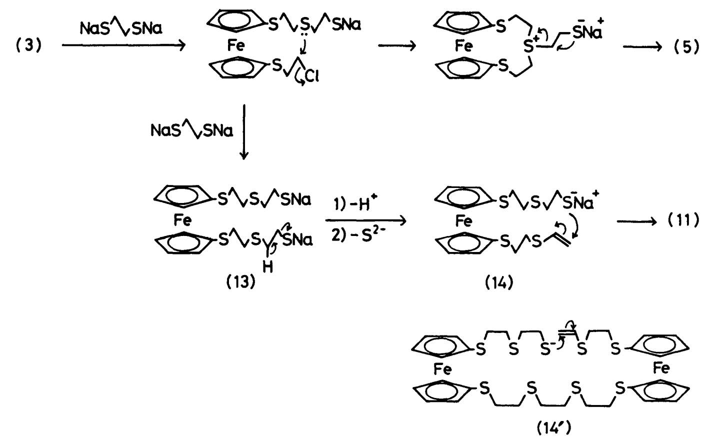


Scheme 1.

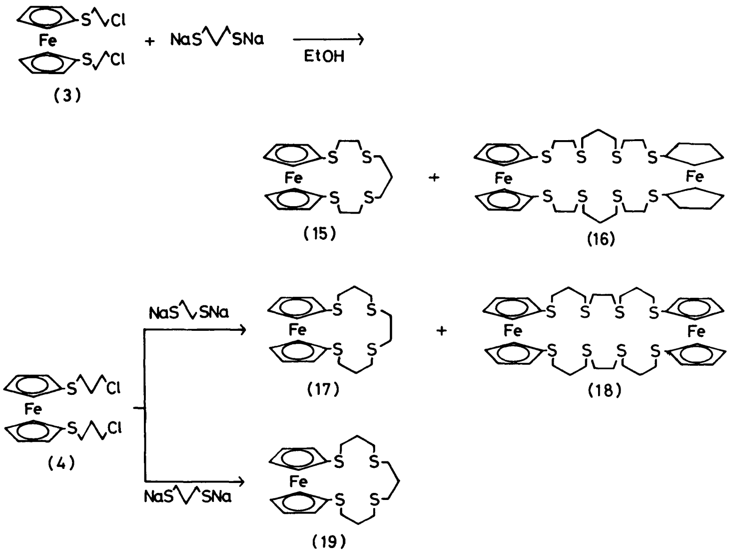


and 1,4,7,10-tetrathia[10]ferrocenophane (**7**) (3.1%). The formation of the abnormal products **2** and **7** may be rationalized in terms of the formation of the intermediate monochloride (**8**) or the dimeric monochloride (**9**) and the following cyclic sulfonium ions as shown in Scheme 1. Similar propagation products are reported in the reaction of bis(2-chloroethyl) ether with sodium sulfide.[14] The replacement of the reaction solvent from ethanol to *N*,*N*-dimethylformamide caused no enhancement of the yield of **5** and **6**. The structure of **5** was confirmed by its ^{1}H-NMR and mass spectra [*m/z* 336 (M$^+$)]. In the ^{1}H-NMR spectrum of **5**, the ring protons and the methylene protons appeared as a pair of triplets at δ 4.25 (4H) and 4.33 (4H), and as a multiplet at δ 2.9—3.5 (8H), respectively. The close appearance of the α- and β-ring protons suggests little tilt-deformation caused by the seven-membered (three sulfur and four carbon atoms) bridging chain. The structure of the dimer **6** was similarly assigned by its mass spectrum [*m/z* 672 (M$^+$)] and ^{1}H-NMR spectrum [δ 4.28 (s, 8H) and δ 2.6—3.2 (m, 8H)]. The methylene protons of the former were observed at somewhat lower field than that of the latter; this is probably because the former methylene portons were held in a deshielding zone between the two cyclopentadienyl rings as described above.

The dichloride **3** reacted with four equivalents of disodium 1,2-ethanedithiolate by refluxing in ethanol–tetrahydrofuran for 2 h. After the usual work-up, the reaction mixture was chromatographed on silica gel by elution with hexane–toluene to give 1,4,7,10-tetrathia[10]-ferrocenophane (**7**) and 1,4,7,10,22,25,28,31-octathia[10.10]-ferrocenophane (**10**) in 50.4 and 3.6% yields, respectively. Moreover, the unexpected products, 1,4,7-trithia[7]ferrocenophane (**5**) (1.7%), 1,4,7,10,13-pentathia[13]ferrocenophane (**11**) (11.6%), and 1,4,7,10,13,25,28,31,34-nonathia[10.13]ferrocenophane (**12**) (1.6%) were isolated. Treatment of **3** with one equivalent of disodium 1,2-ethanedithiolate under similar conditions gave all compounds described above (**5**, **7**, **10**, **11**, and **12**) in yields slightly different from the above experiment. The structure of these compounds was assigned by their elemental analyses, mass, and ^{1}H-NMR spectra. For example, **11** showed the molecular ion (M$^+$) at *m/z* 456 in the mass spectrum. The ^{1}H-NMR spectrum of **11** had the resonances at δ 4.26 (m, 8H) and 2.7—3.2 (m, 16H). The formation of **5** can be rationalized by the intermediate formation of a monochloride followed by a cyclic sulfonium ion as described above (Scheme 2). A similar process was presumed in the reaction of bis(2-chloroethyl) sulfide with the sodium salt of 1,2-ethanedithiol.[5] A possible mechanism for the unexpected formation of **11** and **12** is proposed in Scheme 2. A similar type of reaction has been observed only in the reaction of 1,1′-bis(2-chloroethoxy)ferrocene with disodium 1,2-ethanedithiolate.[15] The initial reaction would be a nucleophilic attack of two moles of disodium 1,2-ethanedithiolate on the halogenated carbons of **3** to form the dithiolate (**13**). Subsequently, one proton elimination from the methylene carbon next to a sulfur atom takes place and is followed by elimination of S^{2-} to give a vinyl sulfide intermediate (**14**). Thus, the formation of **11** can be interpreted by an intramolecular attack of —S$^-$ to the double bond of **14** followed by addition of proton to the resulting sulfur-stabi-



Scheme 2.



lized anion. The formation of **12** can be similarly explained *via* the intermediate (**14′**). The driving force of the unusual propagation reaction may be an easy formation of the sulfur-stabilized carbanion from **13**.

The chloride **3** was treated with four equivalents of disodium 1,3-propanedithiolate in refluxing ethanol–tetrahydrofuran for 2 h under nitrogen. After the usual work-up, the reaction mixture was chromatographed on silica gel to give 1,4,8,11-tetrathia[11]ferrocenophane (**15**) in 57% yield. The ^{1}H-NMR spectrum of **15** showed ferrocene ring protons as a singlet at δ 4.27 (8H), the methylene protons next to a sulfur atom as multiplets at δ 2.7—3.0 (8H) and 3.0—3.2 (4H), and the methylene protons as a quintet at δ 2.02, confirming the assigned structure. On addition to **15**, the compound (**16**), assumed to be the dimer of **15** by its mass and ^{1}H-NMR spectra, was isolated, although the final assignment was unsuccessful because of insufficient product.

1,1′-bis(3-chloropropylthio)ferrocene (**4**) reacted with four molar equivalents of disodium 1,2-ethanedithiolate in similar conditions to those described above, affording 1,5,8,12-tetrathia[12]ferrocenophane (**17**) and 1,5,8,12,24,28,31,35-octathia[12.12]ferrocenophane (**18**) in 47.8% and 11.2% yields, respectively. The reaction with one equivalent of the sodium salt gave considerably decreased yields of the products and no dimer **18**. The reaction of **4** with one equivalent of disodium 1,3-propanedithiolate gave 1,5,9,13-tetrathia[13]ferrocenophane (**19**) in 64.6% yields. The reaction with 4 equivalents of the sodium salt resulted in no increase of the yield of **19** and no isolation of the corresponding dimer.

The electronic and ^{13}C-NMR spectral data of the mononuclear derivatives **2**, **5**, **7**, **11**, **15**, **17**, and **19** were summarized in Tables 1 and 2. As shown in Table 1, 1,4,7-trithia[7]ferrocenophane (**5**) showed an abnormally bathochromic shift ($\Delta\lambda$ *ca.* 20 nm) and an increase in the absorbance ($\Delta\varepsilon$ *ca.* 40) of an absorption band near 440 nm characteristic of ferrocene, which was assigned to d-d transition from the HOMO to the LUMO.[16] In its ^{13}C-NMR spectrum, **5** showed a

TABLE 1. ELECTRONIC SPECTRAL DATA OF MONONUCLEAR FERROCENOPHANES **2**, **5**, **7**, **11**, **15**, **17**, AND **19**

Compd	**2**	**5**	**7**	**11**	**15**	**17**	**19**
$\lambda_{\max}$ (nm)	438	461	442	442	443	443	443
ε	138	272	223	195	196	191	190

TABLE 2. ^{13}C-NMR SPECTRAL DATA OF MONONUCLEAR FERROCENOPHANES **2**, **5**, **7**, **11**, **15**, **17**, AND **19** (22.5 MHz, CDCl$_3$)

Compd	^{13}C-NMR (δ)
2	85.0 (C$_b$), 70.0 (C$_\alpha$), 68.7 (C$_\beta$), 31.1 (SCH$_2$)
5	89.7 (C$_b$), 70.6 (C$_\alpha$), 67.5 (C$_\beta$), 37.2, 32.8 (SCH$_2$)
7	85.3 (C$_b$), 72.1 (C$_\alpha$), 68.9 (C$_\beta$), 38.3, 32.6, 31.1 (SCH$_2$)
11	84.4 (C$_b$), 72.4 (C$_\alpha$), 69.2 (C$_\beta$), 37.2, 33.4, 32.7, 32.3 (SCH$_2$)
15	85.3 (C$_b$), 72.0 (C$_\alpha$), 68.8 (C$_\beta$), 36.8, 31.9, 31.3, 30.4 (SCH$_2$)
17	84.3 (C$_b$), 72.9 (C$_\alpha$), 68.9 (C$_\beta$), 34.9, 32.1, 30.0, 29.1 (SCH$_2$)
19	84.1 (C$_b$), 72.9 (C$_\alpha$), 68.9 (C$_\beta$), 35.0, 30.8, 30.2, 28.9 (SCH$_2$)

down-field shift of the bridgehead carbon resonance ($\Delta\delta$ *ca.* 4 ppm) and an up-field shift of the α- and β-ring carbon resonances ($\Delta\delta$ 0.6—2.3 ppm) of the ferrocene necleus, compared with those of other cyclophanes. There seems to be no tilting strain of the two cyclopentadienyl rings in this molecule, since only a slight splitting of the chemical shifts of the α- and β-ring protons was observed as described previously. The stereomolecular model also evidenced the absence of a tilting strain in **5**. The abnormal shifts observed in the electronic and ^{13}C-NMR spectra therefore may be interpreted by an interaction either between a ferrocene nucleus and a sulfur atom in the 4-position or between a ferrocene nucleus and sulfur atoms in the 1- and 7-positions of **5**. The former possibility, however, is excluded by the fact that such an abnormal shift was not observed in the electronic and ^{13}C-NMR spectra of 1,7-dioxa-4-thia[7]ferrocenophane.[17] From consideration of the stereomolecular model of **5**, the hybrid orbital of the lone pair of the sulfur atom attached to the cyclopentadienyl rings is held to be perpendicular to the plane of cyclopentadienyl rings. Two possible interactions, therefore, remain to explain the spectroscopic characteristics observed in **5**: an interaction between the nonbonding d-orbital on the iron atom and the lone pair of a sulfur atom and an interaction between the lone pair of a sulfur atom and the Fe–C bond connecting a cyclopentadienyl ring to an iron atom (σ–π conjugation).[18] The detailed study on this phenomena will be discussed in another paper.[19]

Experimental

Materials. 1,1′-Ferrocenedithiol was prepared from 1,2,3-trithia[3]ferrocenophane.[11] 1,2-Dibromoethane, 1-bromo-2-chloroethane, 1-bromo-3-chloropropane, 1,2-ethanedithiol and 1,3-propanedithiol were all commercially available; the purity of the last two was checked by GLC. All reactions were done under an atmosphere of nitrogen.

1,4-Dithia[4]ferrocenophane (2). To a suspension of 1,1′-ferrocenedithiol (0.34 g, 1.4 mmol) in ethanol (50 ml) was added a 40% aq solution of sodium hydroxide (0.23 ml) under stirring. The resulting red solution of disodium 1,1′-ferrocenedithiolate (**1**) and a solution of 1,2-dibromoethane (0.12 ml, 1.4 mmol) in ethanol (50 ml) were added dropwise at the same rate to N$_2$-saturated ethanol (100 ml) for a period of 3 h under stirring at room temperature, and then further stirred overnight. After the reaction had been completed, the mixture was evaporated under vacuum, the residue was dissolved in benzene and the undissolved material was filtered off. Chromatography of the condensed filtrate on silica gel gave 1,4-dithia[4]ferrocenophane (**2**) (0.14 g, 37%) as orange cubes, mp 138—139 °C. Found: C, 52.18; H, 4.34%. Calcd for $C_{12}H_{12}S_2Fe$: C, 52.18; H, 4.38%. MS (75 eV); *m/z* 276 (M$^+$, 100%) and 248 (M$^+$−CH$_2$CH$_2$, 57%). IR (KBr): 3080, 1410, 1160, 1020, 890, and 810 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=3.33 (s, 4H, CH$_2$CH$_2$), 4.19 (t, 4H, J=1.9 Hz, H$_\alpha$), and 4.41 (t, 4H, J=1.9 Hz, H$_\beta$).

1,1′-Bis(2-chloroethylthio)ferrocene (3). To a solution of disodium 1,1′-ferrocenedithiolate (**1**), prepared from 1,1′-ferrocenedithiol (0.50 g, 2 mmol) and 40% aq sodium hydroxide (0.4 ml) in ethanol (40 ml), was all at once added a solution of 1-bromo-2-chloroethane (0.63 g, 4.4 mmol) in ethanol (2 ml). The solution was stirred for 4 h at room temperature. After the reaction mixture had been evaporated under vacuum, the residue was chromatographed on silica gel by elution of hexane–toluene (2:1), giving 1,1′-bis(2-chloroethylthio)ferrocene (**3**) as orange crystals (0.45 g, 61%), mp 90.5—91 °C, along with a trace amount (4%) of 1,4-dithia[4]ferrocenophane (**2**). Found: C, 45.05; H, 4.10%. Calcd for $C_{14}H_{16}Cl_2S_2Fe$: C, 44.82; H, 4.30%. MS (75 eV):*m/z* 375 (M$^+$, 100%) and 276 (M$^+$−C$_2$H$_4$Cl$_2$, 32%). IR (KBr): 3080, 1438, 1210, 1020, 983, 828, and 690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=2.86 (t, 4H, J=8.7 Hz, CH$_2$S), 3.57 (t, 4H, J=8.7 Hz, CH$_2$Cl) 4.29 (t, 4H, J=1.7 Hz), 4.35 (t, 4H, J=1.7 Hz).

1,1′-Bis(3-chloropropylthio)ferrocene (*4*). A similar reaction of 1,1′-ferrocenedithiol (3.83 g, 15.3 mmol), 40% aq sqlution of sodium hydroxide (2.3 ml), and 1-bromo-3-chloropropane (5.78 g, 36.7 mmol) gave 1,1′-bis(3-chloropropylthio)ferrocene (**4**) (4.36 g, 70.7%) as an orange oil. Found: C, 47.59; H, 5.00%. Calcd for $C_{16}H_{20}Cl_2S_2Fe$: C, 47.66; H, 5.01%. MS (75 eV): *m/z* 402 (M$^+$, 100%). IR (Neat): 3080, 2950, 1440, 1420, 1268, 1020, and 825 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=1.94 (m, 4H, CH$_2$), 2.71 (t, 4H, J=6.8 Hz, CH$_2$S), 3.61 (t, 4H, J=6.4 Hz, CH$_2$Cl), 4.24 (t, 4H, J=1.8 Hz), and 4.30 (t, 4H, J=1.8 Hz).

Reaction of 1,1′-Bis(2-chloroethylthio)ferrocene (3) with Sodium Sulfide. To a solution of sodium sulfide nonahydrate (0.54 g, 2.2 mmol) in anhyd. ethanol (250 ml) was added a solution of 1,1′-bis(2-chloroethylthio)ferrocene (**3**) (0.67 g, 1.8 mmol) in tetrahydrofuran (THF) (45 ml). The solution was refluxed for 10 h under nitrogen. After the reaction had been completed, the reaction mixture was evaporated under vacuum, the residue was dissolved in benzene and the yellow precipitate was filtered off. The filtrate was condensed and chromatographed on silica gel by elution with hexane–toluene, the following products being separated and purified by recrystallization. 1,4-Dithia[4]ferrocenophane (**2**) (0.025 g, 5%). 1,4,7-Trithia[7]ferrocenophane (**5**) (0.17 g, 28%) as red plates, mp 120 °C. Found: C, 50.10; H, 4.89%. Calcd for $C_{14}H_{16}S_3Fe$: C, 50.00; H, 4.80%. MS (75 ev): *m/z* 336 (M$^+$, 100%), 280 (M$^+$−2C$_2$H$_4$, 44%), 248 (24%), and 184 (44%). IR (KBr): 3080, 1418, 1160, 1020, and 806 cm^{-1}.

^{1}H-NMR (CDCl$_3$): δ=3.0—3.5 (m, 8H, CH$_2$S), 4.28 (m, 8H, ring-H). 1,4,7,10-Tetrathia[10]ferrocenophane (**7**) (0.22 g, 3.1%) (See later.). 1,4,7,19,22,25-Hexathia-[7.7]ferrocenophane (**6**) (0.039 g, 6.5%) as yellow orange crystals, mp 185—185.5 °C. Found: 50.13; H, 4.79%. Calcd for C$_{28}$H$_{32}$S$_6$Fe$_2$: C, 50.00; H, 4.80%. MS (75 eV): *m/z* 672 (M$^+$, 14%), 336 (M$^+$/2, 23%), and 304 (M$^+$/2-S, 100%). IR (KBr) 3080, 1418, 1190, 1022, and 810 cm^{-1}. ^{1}H-NMR (CDCl$_3$):δ=2.6—3.2 (m, 16H, CH$_2$S) and 4.28 (s, 16H).

The same reaction was carried out using *N,N*-dimethylformamide in the place of ethanol–THF as a solvent to give **5** and **6** in 27.2 and 9.1% yields, respectively.

Reaction of 1,1′-Bis(2-chloroethylthio)ferrocene (3) with Disodium 1,2-Ethanedithiolate. To a solution of sodium hydroxide (1.2 g, 30 mml) in anhyd ethanol (400 ml) was added 1,2-ethanedithiol (1.0 ml, 12 mmol), and then all at once a solution of 1,1′-bis(2-chloroethylthio)ferrocene (**3**) (1.12 g, 3 mmol) in anhyd THF (75 ml). The resulting solution was gently refluxed for 2 h and then evaporated under vacuum. Water was added, the mixture was extracted with benzene and the benzene extract was dried over anhyd. sodium sulfate and evaporated. The residue was chromatographed on silica gel to give the following products: 1,4,7-Trithia[7]ferroceneophane (**5**) (0.017 g, 1.7%). 1,4,7,10-Tetrathia[10]ferrocenophane (**7**) (0.60 g, 50.5%) as orange crystals, mp 116 °C. Found: C, 48.61; H, 4.97%. Calcd for C$_{16}$H$_{20}$S$_4$Fe: C, 48.48; H, 5.09%. MS (75 eV): *m/z* 396 (M$^+$, 100%), 272 (M$^+$—124, 61%) and 184 (18%). IR (KBr): 3075, 1420, 1268, 1020, 800, and 688 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=2.7—3.0 (m, 4H, CH$_2$S), 3.0—3.3 (m, 4H, CH$_2$S), 3.10 (s, 4H, SCH$_2$-CH$_2$S), and 4.25 (m, 8H, ring-H).

1,4,7,10,13-Pentathia[13]ferrocenophane (**11**)(0.159 g, 11.6%) as orange needles, mp 100.5—102 °C. Found: C, 47.49; H, 5.44%. Calcd for C$_{18}$H$_{24}$S$_5$Fe: C, 47.36; H, 5.30%. MS (75 eV): *m/z* 456 (M$^+$, 100%), 332 (M$^+$—124), 272 (13%), and 184 (11%). IR (KBr): 3070, 1420, 1195, 1025, and 820 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=2.7—3.2 (m, 16H, CH$_2$S) and 4.26 (s, 8H, ring-H).

1,4,7,10,22,24,27,30-Octathia[10,10]ferrocenophane (**10**) (0.043 g, 3.6%) as reddish orange crystals, mp 152.5—153.5 °C. Found: C, 48.48; H, 5.25%. Calcd for C$_{32}$H$_{40}$S$_8$Fe$_2$: C, 48.48; H, 5.09%. MS (25 eV): *m/z* 792 (M$^+$, 100%) and 272 (59%). IR (KBr): 3080, 2920, 1422, 1200, 1020 and 820 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=2.5—3.0 (m, 16H, CH$_2$S), 2.66 (s, 8H, SCH$_2$CH$_2$S), and 4.34 (m, 16H, ring-H).

1,4,7,10,13,25,28,31,34-nonathia[10.13]ferrocenophane (**12**) (0.022 g, 1.6%) as orange crystals, mp 114.5 °C. Found: C, 47.74; H, 5.53%. Calcd for C$_{34}$H$_{44}$S$_9$Fe$_2$: C, 47.88; H, 5.20%. MS (35 eV): *m/z* 852 (M$^+$, 7%) and 272 (100%). IR (KBr): 3080, 2920, 1424, 1188, 1018, and 805 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ= 2.5—3.0 (m, 28H, CH$_2$S) and 4.35 (m, 16H, ring-H).

When one equivalent of disodium 1,2-ethanedithiolate was used in the above reaction, the yields of **5**, **7**, **11**, **10**, and **12** were 6.0, 32.7, 8.6, 2.6, and 1.4%, respectively.

Reaction of 1,1′-Bis(2-chloroethylthio)ferrocene (3) with 1,3-Propanedithiol. To a solution of sodium hydroxide (0.855 g) in anhydrous ethanol (280 ml) was added 1,3-propanedithiol (0.84 ml, 8.4 mmol) and then a solution of 1,1′-bis(2-chloroethylthio) ferrocene (0.748 g, 2 mmol) in anhyd. THF (50 ml) under an atmosphere of nitrogen. The solution was refluxed for 2 h and then evaporated. The residue was chromatographed on silica gel to give two products: 1,4,8,11-tetrathia[11]ferrocenophane (**15**) (0.462 g, 56.3%) as orange plates, mp 75 °C. Found: C, 49.79; H, 5.15%. Calcd for C$_{17}$H$_{22}$S$_4$Fe: C, 49.75; H, 5.40%. MS (75 eV): m/z 410 (M$^+$, 96%), 286 (M$^+$ —124, 100%), 248 (35%), and 184 (16%). IR (KBr): 3080, 2895, 1432, 1262. 1160, 1024, 886, and 805 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=2.02 (p, 2H, *J*=7.5 Hz, CH$_2$), 2.7—3.0 (m, 8H, CH$_2$S), 3.0—3.2 (m, 4H, CH$_2$S), and 4.27 (s, 8H, ring-H).

1,4,8,11,23,26,30,33-Octathia[11.11]ferrocenophane (**16**) as yellow crystals, mp 132 °C. MS (35 eV): *m/z* 820 (M$^+$, 4%), 410 (M$^+$/2, 14%), and 286 (100%). IR (KBr): 3085, 2930, 1622, 1430, 1204, 1025, 895, and 835 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=1.75 (p, 4H, *J*=7.3 Hz, CH$_2$), 2.56 (t, 8H, *J*=7.3 Hz, SCH$_2$), 3.0—2.5 (m, 16H, SCH$_2$), and 4.34 (m, 16H, ring-H).

Reaction of 1,1′-Bis(3-chloropropylthio)ferrocene(4) with 1,2-Ethanedithiol. To a solution of disodium 1,2-ethanedithiolate, prepared from 1,2-ethanedithiol (1.0 ml, 12 mmol) and sodium hydroxide (1.2 g, 30 mmol) in anhyd. ethanol (400 ml) was added a solution of 1,1′-bis(3-chloropropylthio) ferrocene (**4**) (1.21 g, 3 mmol) in anhyd THF (75 ml) under an atmosphere of nitrogen. After being refluxed for 2 h, the solution was evaporated under vacuum, the residue was dissolved in water, the mixture was extracted with benzene, the extract was dried over anhyd. sodium sulfate and then evaporated. From the residue, two crystalline products were isolated by chromatography on silica gel:

1,5,8,12-Tetrathia[12]ferrocenophane (**17**) (0.608 g, 47.8%) as orange crystals, mp 98 °C. Found: C, 51.25; H, 5.70%. Calcd for C$_{18}$H$_{24}$S$_4$Fe: C, 50.93; H, 5.70%. MS (75 eV): *m/z* 424 (M$^+$, 100%) and 184 (19%). IR (KBr): 3080, 2900, 1410, 1248, 1165, 1020, and 812 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=1.91 (m, 4H, CH$_2$), 2.7—3.0 (m, 8H, CH$_2$S), 2.80 (s, 4H, SCH$_2$CH$_2$S), and 4.25 (s, 8H, ring-H).

1,5,8,12,24,28,31,35-Octathia[12.12]ferrocenophane (**18**) (0.143 g, 11,2%) as yellow fine needles, mp 82—83 °C. Found: 51.17; H, 5.79%. Calcd for C$_{36}$H$_{48}$S$_8$Fe$_2$: C, 50.93; H, 5.70%. MS(35 eV): *m/z* 848 (M$^+$, 18%) and 424 (M$^+$/2, 100%). IR (KBr): 2900, 1422, 1240, 1020, and 830 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ=1.82 (p, 8H, *J*=7.3 Hz, CH$_2$), 2.66 (t, 8H, *J*= 7.5 Hz, CH$_2$S), 2.69 (s, 8H, SCH$_2$CH$_2$S), 2.73 (t, 8H, *J*=7.1 Hz, CH$_2$S), 4.2—4.37 (m, 16H, ring-H).

When one equivalent of disodium 1,2-ethanedithiolate was used in the above reaction, **17** was obtained in 35% yield and the dimer **18** was not isolated.

1,5,9,13-Tetrathia[13]ferrocenophane (19). To a solution of disodium 1,3-propanedithiolate, prepared from 1,3-propanedithiol (0.10 ml, 1 mmol) and sodium hydroxide (0.089 g, 2.2 mmol) in anhyd. ethanol (125 ml), was all at once added a solution of 1,1′-bis(3-chloropropylthio)ferrocene (**4**) (0.403 g, 1.0 mmol) in anhyd. THF (26 ml) under nitrogen. The solution was gently refluxed for 5 h and then evaporated under vacuum. The residue was chromatographed on silica gal by elution with hexane-toluene (3:1) to give 1,5,9,13-tetrathia[13]ferrocenophane (**19**) (0.283 g, 64.6%) as orange needles, mp 60 °C. Found: C, 52.20; H, 5.81%. Calcd for C$_{19}$H$_{26}$S$_4$Fe: C, 52.04; H, 5.98%. MS (75 eV): *m/z* 438 (M$^+$, 100%) and 184 (5%). IR (KBr): 3100, 2900, 1415, 1255, 1168, 1020, and 818 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ= 1.7—2.2 (m, 6H, CH$_2$), 2.5—3.0 (m, 12H, SCH$_2$), and 4.25 (s, 8H, ring-H).

Application of 4 equivalents of disodium 1,3-propandithiolate in the above reaction resulted in no increase in the yield of the monomer **19** and no detection of the corresponding dimer.

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