ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 589 (1999) 50–58

Journal of Organometallic Chemistry

Characterization of ferrocene derivatives bearing podand dipeptide chains (-L-Ala-L-Pro-OR)

Toshiyuki Moriuchi, Akihiro Nomoto, Kazuhiro Yoshida, Toshikazu Hirao *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

Received 1 March 1999

Abstract

Ferrocene derivatives bearing podand dipeptide chains (-L-Ala-L-Pro-OR; R = Me, Et, Pr, CH_2Ph) were synthesized and characterized by spectroscopy and X-ray crystallography. The ferrocenes exhibited Cotton effects in the CD spectra to indicate an ordered conformation, which is considered to depend on the intramolecular hydrogen bonds between C=O (Ala) and N–H (Ala of another strand). The X-ray structural analysis also revealed that such identical intramolecular hydrogen bonding is present in the solid state to orient the podand dipeptide chains in the same direction. A helical molecular arrangement in the crystal packing was observed in the case of the methyl and ethyl esters to form the ferrocenic and hydrophobic columns.

Keywords: Crystal packing; Dipeptide; Ferrocene; Helical arrangement; Hydrogen bond

1. Introduction

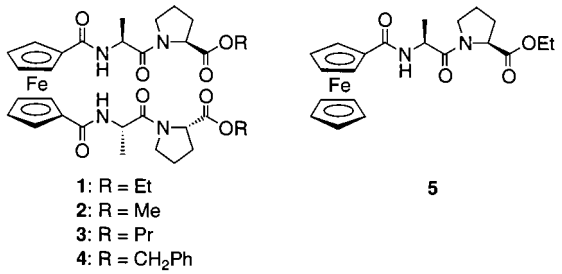
Construction of highly ordered supramolecular systems by self-assembly of a given set of components has been an area of intense interest from the viewpoint of their potential application [1]. Biological systems claim a variety of highly ordered molecular assemblies to fulfill the functions as observed in the double helices of DNA and RNA and α-helices, β-sheets, and β-turns of proteins. The introduction of organometallic moieties into these biomolecules is envisioned to provide new biomaterials or efficient redox systems [2]. Ferrocenes are recognized as an organometallic scaffold for molecular receptors [3] and peptide mimetic models [4] based on two rotatory coplanar cyclopentadienyl rings and redox properties. A short peptide chain possessing chiral centers and hydrogen bonding sites is considered to be a convenient building block to form artificial supramolecules [5]. In this context, we recently embarked upon the incorporation of the podand dipeptide chains, -L-Ala-L-Pro-OEt, into ferrocene, leading to a helical molecular arrangement in the crystal packing of **1** with two intramolecular hydrogen bonds (Scheme 1) [6]. These intriguing results prompted us to investigate further to gain insight into the structural factors for the molecular arrangement. In this paper, we focus on the effect of the ester moieties to elucidate the crystal structure of the ferrocene derivatives bearing podand dipeptide chains (-L-Ala-L-Pro-OR).

2. Results and discussion

An advantage in the use of L-alanyl-L-proline as a dipeptide is the presence of a hydrogen bonding site and a sterically constrained proline as a well-known turn inducer in proteins. The ferrocene derivatives **1**–**4** bearing the podand dipeptide chains, -L-Ala-L-Pro-OR (Scheme 1; R = Et, Me, Pr, CH_2Ph, respectively), were synthesized by condensation of 1,1'-bis(chlorocarbonyl)ferrocene with the corresponding dipeptide esters as shown in Scheme 2. The ferrocenes thus obtained were fully characterized by spectral data and elemental analyses. Compared with the parent ferrocene (0.51 V versus Ag/Ag^+), **1**–**4** exhibited a reversible Fc/Fc^+ redox couple at a more positive value, 0.81 V, due to the electron-withdrawing amide functional groups (Table 1).

* Corresponding author.

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00301-0



Scheme 1.

In the ^{1}H-NMR spectra of **1**–**4** in $CDCl_3$ (1.0×10^{-2} M), only one kind of N–H resonance was detected at a lower field (**1**, 8.96 ppm; **2**, 8.95 ppm; **3**, 8.96 ppm; **4**, 8.95 ppm) than that of the mono-substituted ferrocene **5** (6.66 ppm). The former N–H resonance was not perturbed by the addition of aliquots of DMSO-d_6 to $CDCl_3$ although **5** showed a slight down-field shift (Table 1). Two identical intramolecular hydrogen bonds between the podand dipeptide chains of **1**–**4** appear to be present in solution. Peptidic amide protons, which are locked in a very strong hydrogen bond or are not hydrogen bonded, are known to exhibit a small temperature dependence on the chemical shift (-2 to -4 ppb K^{-1}) [7]. Variable-temperature ^{1}H-NMR studies of **1**–**4** (1.0×10^{-2} M in $CDCl_3$ between 223 and 323 K) showed $\Delta\delta/\Delta T$ values around -3.7 ppb K^{-1}, whereas the $\Delta\delta/\Delta T$ value for **5** was -2.3 ppb K^{-1}. These results support strong hydrogen bonding for **1**–**4**. The vicinal coupling constant J_{NH} in the NH–CH fragment of Ala is 7.3 Hz for **1**–**4** and 6.9 Hz for **5**. Since the C_5 conformer of the alanine residue is known to give ca. 7 Hz as the J_{NH} value [8], the J_{NH} value of **5** suggests a possibility of the C_5 conformation. In the FT-IR spectra (CH_2Cl_2), the absorption of amide N–H appeared differently at around 3300 cm^{-1} (broad intense) for **1**–**4** and at 3415 cm^{-1} for **5**, which are consistent with the above-mentioned observations.

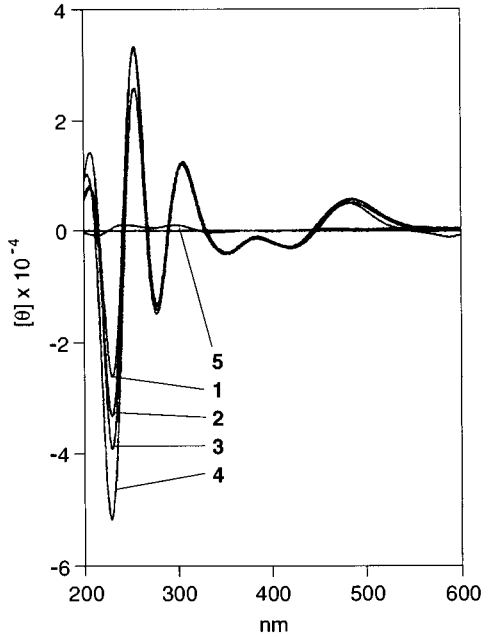
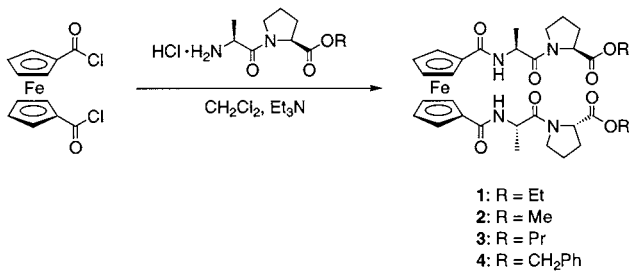


Fig. 1. CD spectra of **1**–**5** in MeCN (1.0×10^{-4} M).

It should be noted that **2**–**4** exhibited Cotton effects similarly as observed in **1** although such effects were not observed with **5** (Fig. 1). The effects attributable to the absorbance of the ferrocene moiety in the UV–vis spectra are probably related to the chirality of the



Scheme 2.

Table 1
Selected spectroscopic data

	^{1}H-NMR, N–H (ppm) [a]		$\Delta\delta/\Delta T$, N–H (ppb K^{-1}) [a]	FT-IR, ν_{N-H} (cm^{-1}) [a]	$E_{1/2}$ (V) [b], Fc/Fc^+
	$CDCl_3$	$CDCl_3$–DMSO-d_6 (9:1)	$CDCl_3$	CH_2Cl_2	
1	8.96	8.95	−3.6	3302	0.81
2	8.95	8.94	−3.6	3300	0.81
3	8.96	8.95	−3.7	3302	0.81
4	8.95	8.94	−3.7	3302	0.81
5	6.66 [c]	6.85 [c]	−2.3 [c]	3415 [c]	0.67

[a] 1.0×10^{-2} M.
[b] V vs. Ag/Ag^+.
[c] 2.0×10^{-2} M.

intramolecularly hydrogen-bonded podand dipeptide chains, indicating that **1**–**4** are present in an ordered conformation in the solution.

Further structural information was obtained by a single-crystal X-ray structure determination. The X-ray crystal structure of **2** was also characterized by the presence of two identical intramolecular hydrogen bonds between C=O (Ala) and N–H (Ala of another strand) (N(1)···O(12), 2.941 Å; H···O(12), 2.10 Å; N(11)···O(2), 3.040 Å; H···O(2), 2.14 Å) as indicated in **1** (Fig. 2, Tables 2–4, Scheme 3). The podand dipeptide chains are arranged in the same direction based on two intramolecular hydrogen bonds, although a wide range of relative orientations is possible depending on the two rotatory cyclopentadienyl rings. The ferrocenes **1** and **2** appear to be in similar conformation in solution since the CD spectra of **1** were similar in both KBr pellet and solution states [6]. The structural parameters are summarized in Table 5. Another interesting feature is that the *gauche*

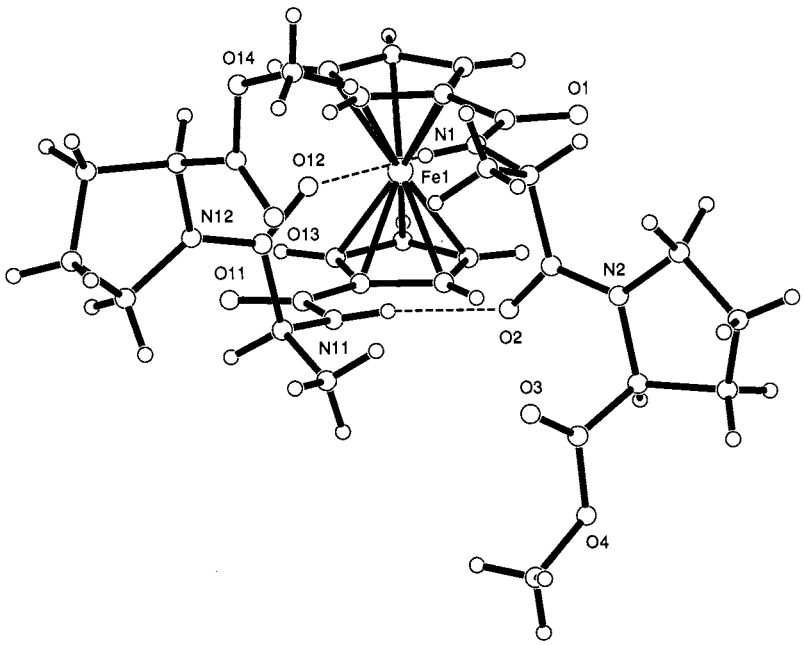


Fig. 2. Molecular structure of **2**.

Table 2
Crystallographic data

	1 [a]	**2**	**3**	**4**	**5** [a]
Formula	$C_{32}H_{42}N_4O_8Fe$	$C_{30}H_{38}N_4O_8Fe$	$C_{34}H_{46}N_4O_8Fe$	$C_{42}H_{46}N_4O_8Fe$	$C_{21}H_{26}N_2O_4Fe$
Molecular weight	666.55	638.50	694.61	790.69	426.29
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$I4_1$, (No. 80)	$P4_3$ (No. 78)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å)	14.978(4)	14.363(5)	17.465(3)	15.900(3)	17.834(3)
b (Å)			19.324(3)	27.020(2)	18.012(2)
c (Å)	14.699(7)	14.909(5)	10.533(3)	9.273(2)	12.623(2)
V (Å^3)	3297(1)	3075(1)	3554(1)	3983(1)	4054.8(8)
Z	4	4	4	4	8
$D_{calc.}$ (g cm^{-3})	1.343	1.379	1.298	1.318	1.397
μ (Mo–K$_\alpha$) (cm^{-1})	5.12	5.45	4.74	4.31	7.72
T (°C)	23	23	23	23	23
λ (Mo–K$_\alpha$) (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
R [b]	0.047	0.051	0.076	0.056	0.056
R_w [c]	0.046	0.034	0.068	0.034	0.025

[a] Further refined data.
[b] $R = \Sigma(|F_o| - |F_c|)/\Sigma |F_o|$.
[c] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 3
Selected bond distances (Å) and angles (°)

	1 [a]	**2**	**3**	**4**	**5** [b]	
Bond distances (Å)						
Fe–C(1)	2.024(7)	2.015(7)	2.021(10)	2.002(9)	2.036(7)	2.027(6)
Fe–C(2)	2.022(8)	2.020(7)	2.02(1)	2.012(10)	2.025(7)	2.054(7)
Fe–C(3)	2.054(8)	2.028(7)	2.059(10)	2.04(1)	2.042(8)	2.029(7)
Fe–C(4)	2.036(7)	2.055(7)	2.030(10)	2.06(1)	2.061(8)	2.040(7)
Fe–C(5)	2.033(7)	2.030(7)	2.013(9)	2.029(10)	2.026(8)	2.005(7)
Fe–C(101)		2.017(7)	2.01(1)	2.01(1)	2.032(8)	2.023(7)
Fe–C(102)		2.027(7)	2.03(1)	2.019(10)	2.042(9)	2.049(8)
Fe–C(103)		2.040(8)	2.04(1)	2.06(1)	2.046(8)	2.040(7)
Fe–C(104)		2.016(8)	2.09(1)	2.07(1)	2.032(9)	2.043(7)
Fe–C(105)		2.020(7)	2.027(10)	2.02(1)	2.029(8)	2.013(8)
C(1)–C(6)	1.478(8)	1.506(9)	1.47(1)	1.51(1)	1.498(9)	1.482(9)
C(101)–C(106)		1.499(9)	1.46(1)	1.48(1)		
C(6)–O(1)	1.222(7)	1.219(7)	1.22(1)	1.22(1)	1.234(7)	1.222(7)
C(106)–O(11)		1.229(6)	1.23(1)	1.22(1)		
C(6)–N(1)	1.348(7)	1.332(8)	1.36(1)	1.33(1)	1.322(9)	1.338(8)
C(106)–N(11)		1.321(7)	1.36(1)	1.33(1)		
N(1)–C(7)	1.453(7)	1.444(8)	1.46(1)	1.46(1)	1.465(9)	1.435(8)
N(11)–C(107)		1.458(7)	1.47(1)	1.45(1)		
Bond angles (°)						
C(2)–C(1)–C(6)	123.0(5)	123.4(6)	122(1)	123(1)	128.0(8)	123.6(8)
C(102)–C(101)–C(106)		128.9(6)	129(1)	130(1)		
C(5)–C(1)–C(6)	129.2(6)	128.7(6)	131.0(10)	127(1)	124.5(8)	130.3(8)
C(105)–C(101)–C(106)		123.5(6)	123(1)	124(1)		
C(l)–C(6)–N(1)	116.3(5)	116.3(6)	117(1)	117(1)	116.6(7)	116.5(7)
C(101)–C(106)–N(11)		117.6(6)	119.8(10)	116(1)		
O(l)–C(6)–N(1)	121.7(6)	121.7(7)	119(1)	121 (1)	122.8(7)	122.1(7)
0(11)–C(106)–N(11)		122.5(6)	116(1)	121(1)		
C(6)–N(1)–C(7)	121.6(5)	122.2(6)	121.1(10)	120.2(10)	121.5(7)	120.5(7)
C(106)–N(11)–C(107)		121.7(5)	122.1(9)	119(1)		

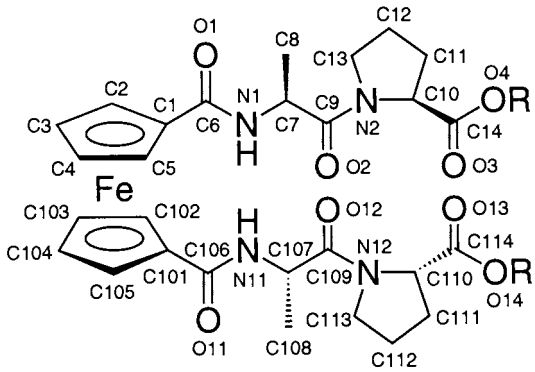
[a] The molecule sits on an inversion center.
[b] Two independent molecules exist in the asymmetric unit.

Table 4
Hydrogen bonds

Crystal	Type [a]	Donor	Acceptor	D···A (Å)	H···A (Å)	D–H···A (°)
1 [b]	Intra	N(1)	O(12)	3.000(6)	2.13(5)	161(5)
2	Intra	N(1)	O(12)	2.941(4)	2.10(2)	164(3)
	Intra	N(11)	O(2)	3.040(4)	2.14(2)	165(2)
3	Intra	N(1)	O(12)	3.030(9)	2.22(5)	161(5)
	Intra	N(11)	O(2)	2.952(9)	2.08(5)	175(5)
4	Intra	N(1)	O(12)	2.925(9)	1.88(5)	178(4)
	Intra	N(11)	O(2)	3.023(9)	2.15(6)	172(6)
5 [c]	Inter	N(1)	O(1a)	3.028(7)	2.13(6)	171(6)
	Inter	N(1a)	O(1)	3.036(7)	2.17(6)	166(5)

[a] Inter, intermolecular; intra, intramolecular.
[b] The molecule sits on an inversion center.
[c] Two independent molecules exist in the asymmetric unit.

eclipsed orientation of two cyclopentadienyl rings of **1** (78.15°) and **2** (75.62°) is accompanied with intramolecular hydrogen bonding to minimize the β-angle defined as the angle between the cyclopentadienyl ring plane and the C(*ipso*)–CO bond. Although the molecule sits on an inversion center in the crystal structure of **1**, the torsion angles of **2** showed a slightly different conformation for the podand dipeptide chains (Table 6). Also,



Scheme 3.

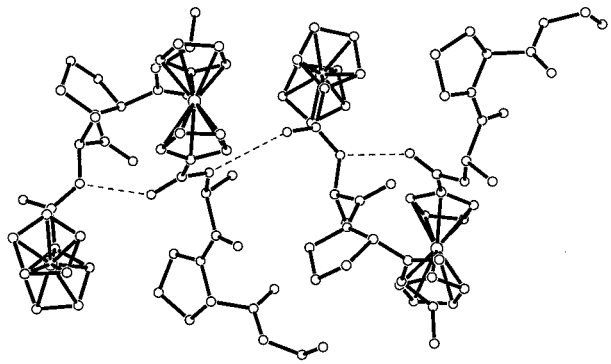


Fig. 3. Crystal packing of **5**.

Table 5
Selected structural parameters

	1 [a]	**2**	**3**	**4**	**5** [b]
Structural parameters					
θ (°) [c]	2.45	0.53	1.75	2.60	3.01, 3.81
β (°) [d]	5.27	3.77, 5.64	1.70, 4.38	2.64, 2.84	22.50, 24.30
ω (°) [e]	78.15	75.62	69.26	74.58	

[a] The molecule sits on an inversion center.
[b] Two independent molecules exist in the asymmetric unit.
[c] The dihedral angle between two cyclopentadienyl rings.
[d] The angle between the plane of cyclopentadienyl ring and C(*ipso*)–CO bond.
[e] The torsion angle defined as C(l)–C(centroid)–C(centroid)–C(101).

two identical intramolecular hydrogen bonds require rotation of the peptide chain, resulting in the observed torsion angles (**1**: $\phi_1 = -86.0°$, $\psi_1 = 159.9°$, **2**: $\phi_1 = -80.2°$, $\psi_1 = 160.1°$, $\phi_1^* = -81.6°$, $\psi_1^* = 153.7°$). The torsion angle ω_1 (167.4° for **1**, 173.7 and 168.7° for **2**) indicates a nearly *trans* conformation of the Pro moiety. The ferrocene **5** bearing only one dipeptide chain exhibited intermolecular hydrogen bonds between C=O (Ala) and N–H (Ala of another molecule) (N(1)···O(1a), 3.028 Å; H···O(1a), 2.13 Å; N(1a)···O(1), 3.036 Å; H···O(2), 2.17 Å), wherein two independent molecules exist in the asymmetric unit and are connected alternately to form an intermolecular hydrogen-bonding network without the C_5 conformation observed in the solution (Fig. 3).

As observed in **1** [6], the ferrocene **2** also showed a helical molecular arrangement with one turn of 14.91 Å pitch height in the crystal packing as shown in Fig. 4(a), where the distance between the nearest ferrocene units is 4.39 Å (Table 7). Furthermore, the ferrocene moieties are arranged in a herringbone motif, and the

Table 6
Torsion angles (°)

	Angle [a]	**1** [b]	**2**	**3**	**4**	**5** [c]	
ϕ_1	C(6)–N(1)–C(7)–C(9)	−86.0(6)	−80.2(7)	−72(1)	−72(1)	−97.7(9)	−75.3(9)
ψ_1	N(1)–C(7)–C(9)–N(2)	159.9(5)	160.1(5)	154.6(10)	147.2(9)	152.5(7)	153.6(7)
ω_1	C(7)–C(9)–N(2)–C(10)	167.4(5)	173.7(5)	−177(1)	178.4(9)	170.0(6)	176.5(7)
ϕ_2	C(9)–N(2)–C(10)–C(14)	−64.9(7)	−70.9(7)	−66(1)	−65(1)	−65.7(9)	−56.8(10)
ψ_2	N(2)–C(10)–C(14)–O(4)	157.0(5)	167.3(5)	144(1)	157.0(9)	−31.7(9)	150.6(7)
ϕ_1^*	C(106)–N(11)–C(107)–C(109)		−81.6(7)	−74(1)	−77(1)		
ψ_1^*	N(11)–C(107)–C(109)–N(12)		153.7(5)	146.4(9)	153.1(9)		
ω_1^*	C(107)–C(109)–N(12)–C(110)		168.7(5)	174(1)	169.5(9)		
ϕ_2^*	C(109)–N(12)–C(110)–C(114)		−68.9(7)	−70(1)	−61(1)		
ψ_2^*	N(12)–C(110)–C(114)–O(14)		165.4(5)	155(1)	154.5(8)		

[a] Symbol used for torsion angles in peptides (IUPAC–IUB Commission on Biochemical Nomenclature).
[b] The molecule sits on an inversion center.
[c] Two independent molecules exist in the asymmetric unit.

proline and methyl ester moieties individually form the columns (Fig. 4b). The podand dipeptide chains are considered to induce such molecular aggregation through a hydrogen bonding site (Ala) and a hydrophobic moiety (Pro). The column size of the ester moieties defined by the distances between the iron centers depends on the ester moieties as shown in Figs. 4(b), 5 and Table 7. The square and rectangle columns are observed for **1** and **2**, respectively, due to the steric effect of the ester moieties on the crystal packing.

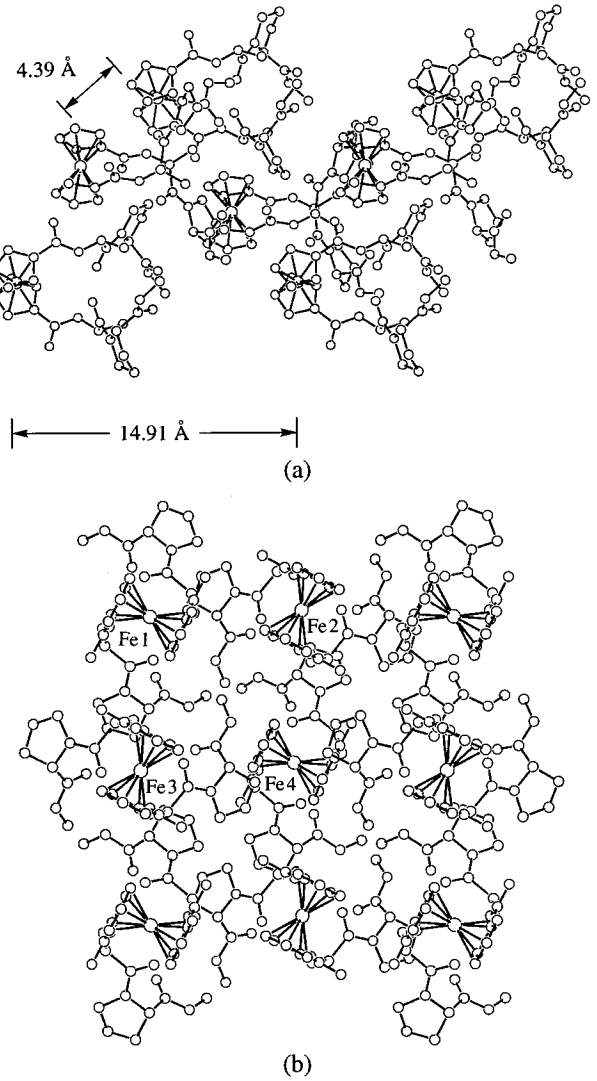


Fig. 4. Crystal packing of **2**: (a) top view of a portion of a layer containing the helical arrangement; (b) side view.

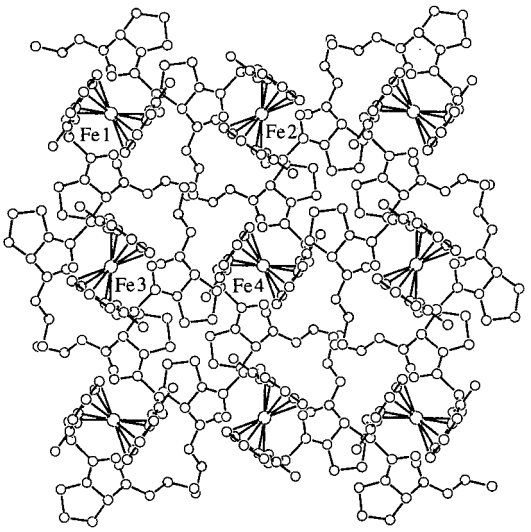


Fig. 5. Crystal packing of **1**.

The crystal analysis of **3** (Fig. 6) and **4** (Fig. 7) bearing the propoxycarbonyl and benzyloxycarbonyl groups, respectively, showed a structure similar to **2**, as observed in structural parameters and torsion angles (Tables 5 and 6) based on two identical intramolecular hydrogen bonds between C=O (Ala) and N–H (Ala of another strand) (**3**: N(1)···O(12), 3.030 Å; H···O(12), 2.22 Å; N(11)···O(2), 2.952 Å; H···O(2), 2.08 Å; **4**: N(1)···O(12), 2.925 Å; H···O(12), 1.88 Å; N(11)···O(2), 3.023 Å; H···O(2), 2.15 Å). On the contrary, a helical molecular arrangement was not induced in the crystal packing. The propyl and benzyl moieties are considered to deform the crystal packing, probably due to their bulkiness. The crystal packing is influenced by the difference in the ester moieties, whereas the molecular conformation is not changed.

In conclusion, the ferrocenes **1**–**4** bearing podand dipeptide chains are present in an ordered conformation in both solution and solid states. The intramolecular hydrogen bonding between C=O (Ala) and N–H (Ala of another strand) of the -L-Ala-L-Pro chains contributes to this conformation. A helical molecular arrangement is observed in the crystal packing of **1** and **2** to form the redox-active ferrocenic and hydrophobic columns. These results present a versatile route to a supramolecular redox system in crystal engineering.

Table 7
Selected distances (Å) in the crystal packing

	1	**2**
Pitch height	14.70	14.91
Distance between the nearest ferrocene units	4.54	4.39
The column size of the ester moieties defined by the distance between iron centers [a]	12.89 12.89	12.17 13.03

[a] Fe(1)–Fe(4) and Fe(2)–Fe(3).

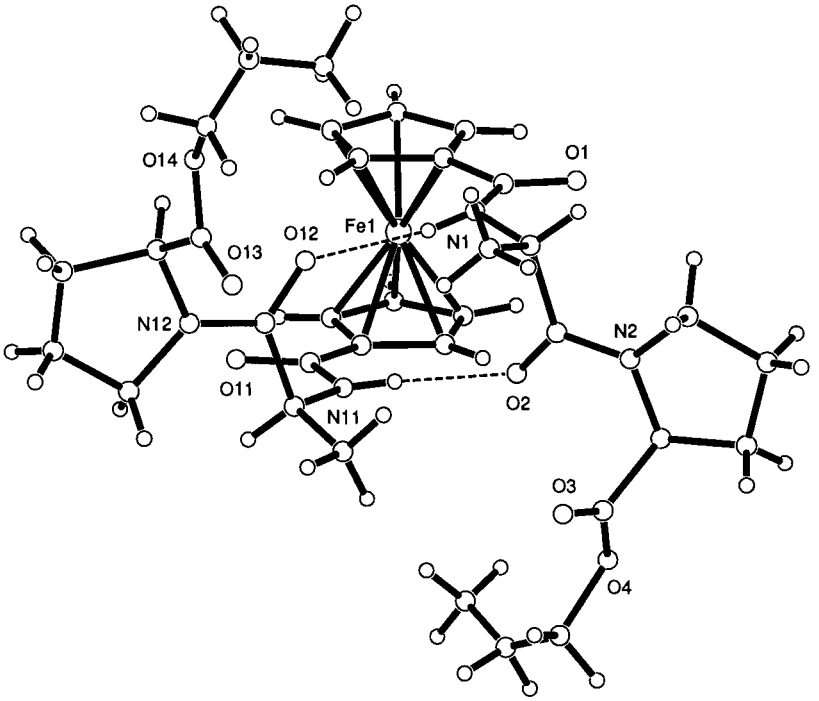


Fig. 6. Molecular structure of **3**.

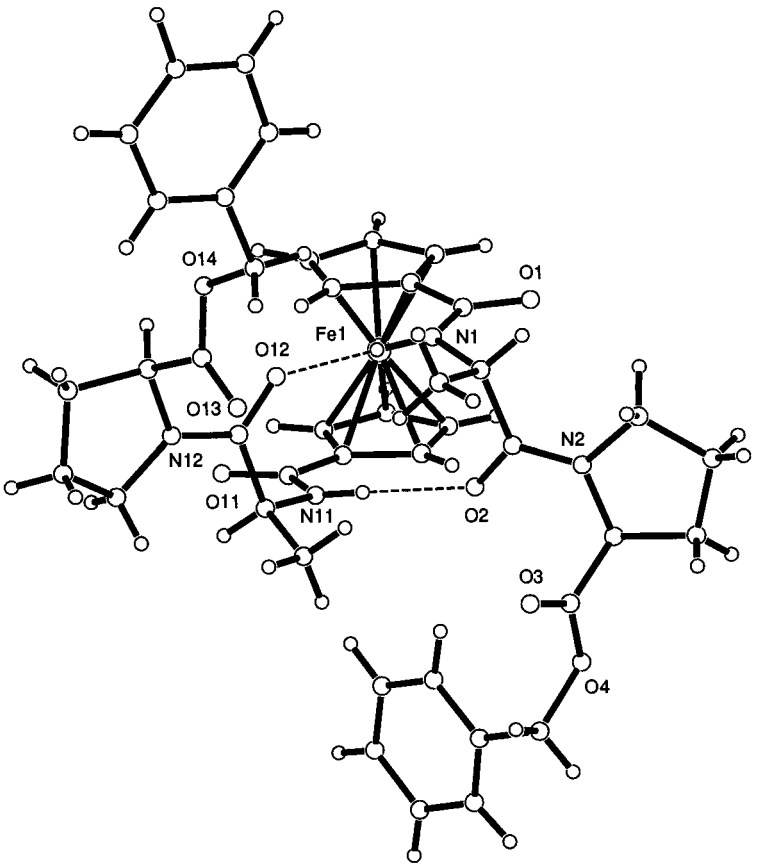


Fig. 7. Molecular structure of **4**.

3. Experimental

All reagents and solvents were purchased from commercial sources and if necessary, purified by the standard methods. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a Perkin–Elmer model 1605 FT-IR. ^{1}H-NMR spectra were recorded on a Varian Unity Inova 600 (600 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a Varian Mercury 300 (75 MHz) spectrometer. Mass spectra were run on a Jeol JMS-DX303HF mass spectrometer. Peptide ester hydrochlorides were prepared by esterification of the commercially available dipeptide, L-alanyl-L-proline, with an alcohol under acidic conditions.

3.1. General procedure for the synthesis of ferrocene derivatives bearing the podand dipeptide chains

To a stirred mixture of H-Ala-Pro-OR·HCl (0.6 mmol) and triethylamine (418 μl, 3.0 mmol) in dichloromethane (4 ml) was added drop-wise 1,1′-bis-(chlorocarbonyl)ferrocene (0.093 g, 0.3 mmol) in dichloromethane (6 ml) under argon at 0°C. The mixture was stirred at 0°C for 1 h and then at room temperature for 1 h. The resulting mixture was diluted with dichloromethane, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was chromatographed on alumina column eluting with dichloromethane. The ferrocene was isolated by recrystallization from dichloromethane–ethyl acetate.

3.1.1. Fc(CO-L-Ala-L-Pro-OMe)$_2$ (**2**)

Orange crystals: 83% yield. M.p. 283–284°C (uncorrected). IR (KBr, cm^{-1}): 3300 (N–H), 1747 (C=O), 1634 (C=O). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.95 (d, 2H, $J = 7.3$ Hz), 4.94–4.93 (m, 2H), 4.88–4.87 (m, 2H), 4.84 (quint, 2H, $J = 7.3$ Hz), 4.65 (dd, 2H, $J = 8.5$, 4.2 Hz), 4.52–4.51 (m, 2H), 4.29–4.28 (m, 2H), 3.93–3.89 (m, 2H), 3.72–3.68 (m, 8H), 2.34–2.28 (m, 2H), 2.14–2.08 (m, 4H), 2.04–1.99 (m, 2H), 1.37 (d, 6H, $J = 7.3$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 173.3, 172.5, 171.7, 75.6, 71.8, 71.0, 70.3, 59.0, 52.1, 47.3, 46.7, 28.9, 25.1, 14.8. MS (FAB): m/z: 639 ($M + 1$). Anal. Calc. for $C_{30}H_{38}N_4O_8Fe$: C, 56.43; H, 6.00; N, 8.78. Found: C, 56.66; H, 5.96; N, 8.76.

3.1.2. Fc(CO-L-Ala-L-Pro-OPr)$_2$ (**3**)

Orange crystals: 73% yield. M.p. 221–222°C (uncorrected). IR (KBr, cm^{-1}): 3302 (N–H), 1745 (C=O), 1631 (C=O). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.96 (d, 2H, $J = 7.3$ Hz), 4.95–4.94 (m, 2H), 4.88–4.87 (m, 2H), 4.84 (quint, 2H, $J = 7.3$ Hz), 4.64 (dd, 2H, $J = 8.4$, 4.2 Hz), 4.51–4.50 (m, 2H), 4.29–4.28 (m, 2H), 4.08–4.04 (m, 2H), 4.02–3.98 (m, 2H), 3.94–3.90 (m, 2H), 3.72–3.68 (m, 2H), 2.34–2.28 (m, 2H), 2.14–2.08 (m, 4H), 2.04–1.99 (m, 2H), 1.65 (sext, 4H, $J = 7.3$ Hz), 1.37 (d, 6H, $J = 7.3$ Hz), 0.94 (t, 6H, $J = 7.3$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 173.3, 171.9, 170.4, 75.7, 71.7, 70.9, 70.2, 66.5, 59.1, 47.3, 46.6, 28.9, 25.0, 22.0, 14.8, 10.4. MS (FAB): m/z: 695 [M + 1]. Anal. Calc. for $C_{34}H_{46}N_4O_8Fe$: C, 58.79; H, 6.68; N, 8.07. Found: C, 58.61; H, 6.64; N, 8.07.

3.1.3. Fc(CO-L-Ala-L-Pro-OCH$_2$Ph)$_2$ (**4**)

Orange crystals: 89% yield. M.p. 212–213°C (uncorrected). IR (KBr, cm^{-1}): 3302 (N–H), 1741 (C=O), 1636 (C=O). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.95 (d, 2H, $J = 7.3$ Hz), 7.36–7.29 (m, 10H), 5.23–5.21 (d, 2H, $J = 12.2$ Hz), 5.06–5.04 (d, 2H, $J = 12.2$ Hz), 4.99–4.98 (m, 2H), 4.90–4.89 (m, 2H), 4.81 (quint, 2H, $J = 7.3$ Hz), 4.70 (dd, 2H, $J = 8.4$, 4.2 Hz), 4.53–4.52 (m, 2H), 4.30–4.29 (m, 2H), 3.93–3.89 (m, 2H), 3.70–3.68 (m, 2H), 2.33–2.28 (m, 2H), 2.13–2.08 (m, 4H), 2.04–2.01 (m, 2H), 1.30 (d, 6H, $J = 7.3$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 173.4, 171.7, 170.4, 135.5, 128.5, 128.1, 127.7, 75.7, 71.8, 70.9, 70.2, 70.1, 66.5, 59.1, 47.4, 46.7, 28.9, 25.1, 14.8. MS (FAB): m/z: 791 [M + 1]. Anal. Calc. for $C_{42}H_{46}N_4O_8Fe$: C, 63.80; H, 5.86; N, 7.09. Found: C, 63.59; H, 5.83; N, 7.12.

3.2. Electrochemical experiments

The cyclic voltammetry measurements were performed on a BAS CV-50 W voltammetry analyzer in the deaerated dichloromethane solution ([ferrocene] = 1.0×10^{-3} M) containing 0.1 M ^{n}Bu$_4$NClO$_4$ as a supporting electrolyte at 25°C with a three-electrode system consisting of a highly polished glassy carbon working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/AgCl reference electrode (BAS) with scan rate 100 mV s^{-1}. Potentials were recorded versus aqueous Ag/AgCl and are not corrected for the junction potential. In the same solvent system, the $E_{1/2}$ value for the ferrocene/ferrocenium redox couple was + 0.51 V with 0.13 V peak separation.

3.3. CD measurements

CD spectra were recorded using a Jasco J-720 spectropolarimeter in the deaerated acetonitrile solution with the concentration (1.0×10^{-4} M) under argon at 25°C.

3.4. X-ray structure analysis

X-ray measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo–K_α

radiation and a rotating anode generator. The data were collected at a temperature of 23 ± 1°C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.1°. The data of **1** and **5** were further refined [6]. The structure of **2** was solved by direct methods and expanded using Fourier techniques. The structures of **3** and **4** were solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 2.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-118017 for **2**, CCDC-118018 for **3**, and CCDC-118019 for **4**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit @ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported in part by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of NMR and MS instruments.

References

[1] (a) J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304. (b) G.M. Whitesides, E.E. Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen, D.M. Gordon, Acc. Chem. Res. 28 (1995) 37. (c) D.S. Lawrence, T. Jiang, M. Levett, Chem. Rev. 95 (1995) 2229. (d) D. Philip, J.F. Stoddart, Angew. Chem. Int. Ed. Engl. 35 (1996) 1154. (e) P.J. Stang, B. Olenyuk, Acc. Chem. Res. 30 (1997) 502. (f) C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 2005.

[2] (a) D.G. McCafferty, B.M. Bishop, C.G. Wall, S.G. Hughes, S.L. Mecklenberg, T.J. Meyer, B.W. Erickson, Tetrahedron 51 (1995) 1093. (b) R.C. Mucic, M.K. Herrlein, C.A. Mirkin, R.L. Letsinger, Chem. Commun. (Cambridge) (1996) 555. (c) T. Ihara, M. Nakayama, M. Murata, K. Nakano, M. Maeda, Chem. Commun. (Cambridge) (1997) 1609. (d) S. Takenaka, Y. Uto, M. Takagi, H. Kondo, Chem. Lett. (1998) 989.

[3] (a) T. Saji, I. Kinoshita, J. Chem. Soc. Chem. Commun. (1986) 716. (b) J.C. Medina, C. Li, S.G. Bott, J.L. Atwood, G.W. Gokel, J. Am. Chem. Soc. 113 (1991) 366. (c) J.C. Medina, T.T. Goodnow, M.T. Rojas, J.L. Atwood, B.C. Lynn, A.E. Kaifer, G.W. Gokel, J. Am. Chem. Soc. 114 (1992) 10583. (d) P.D. Beer, Chem. Commun. (Cambridge) (1996) 689. (e) P.D. Beer, A.R. Graydon, A.O.M. Johnson, D.K. Smith, Inorg. Chem. 36 (1997) 2112.

[4] (a) H. Eckert, C. Seidel, Angew. Chem. Int. Ed. Engl. 25 (1986) 159. (b) R.S. Herrick, R.M. Jarret, T.P. Curran, D.R. Dragoli, M.B. Flaherty, S.E. Lindyberg, R.A. Slate, L.C. Thornton, Tetrahedron Lett. 37 (1996) 5289. (c) M. Kira, T. Matsubara, H. Shinohara, M. Sisido, Chem. Lett. (1997) 89. (d) H.-B. Kraatz, J. Lusztyk, G.D. Enright, Inorg. Chem. 36 (1997) 2400. (e) T. Okamura, K. Sakauye, N. Ueyama, A. Nakamura, Inorg. Chem. 37 (1998) 6731.

[5] N. Ohata, H. Masuda, O. Yamauchi, Angew. Chem. Int. Ed. Engl. 35 (1996) 531.

[6] A. Nomoto, T. Moriuchi, S. Yamazaki, A. Ogawa, T. Hirao, Chem. Commun. (Cambridge) (1998) 1963.

[7] C.N. Kirsten, T.H. Schrader, J. Am. Chem. Soc. 119 (1997) 12061.

[8] M.T. Cung, M. Marraud, J. Néel, J. Chim. Phys. Phys. Chim. Biol. 73 (1976) 213.