Intramolecular Conformational Control in Ferrocenes Bearing Podand Dipeptide Chains

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Ferrocenes bearing podand dipeptide chains were demonstrated to induce intramolecular conformational regulation through hydrogen bondings. The single-crystal X-ray structure determination of the ferrocene bearing the podand dipeptide chains -Gly-L-Pro-OEt confirmed the formation of two intramolecular interchain hydrogen bondings between CO (Gly) and NH (another Gly) of each podand dipeptide chain (N(1)···O(102), 2.910 Å; N(101)···O(2), 2.898 Å; N(201)···O(302), 2.85 Å; N(301)···O(202), 2.87 Å) to give a 10-membered hydrogen-bonded ring. The ferrocene bearing the podand dipeptide chains -L-Pro-Gly-OEt is also considered to form two rigid intramolecular interchain hydrogen bondings between CO (bridging) and NH (another Gly) to give a 14-membered hydrogen-bonded ring. Such an ordered conformation was supported by the induced circular dichroism. On the other hand, the ferrocene bearing one dipeptide chain -Gly-L-Pro-OEt is packed in a helically ordered arrangement with one turn of 15.65 Å pitch height through a network of intermolecular hydrogen bonds, within which the distance between the closest ferrocene units is 7.95 Å (Fe−Fe).

Introduction

The potential utilization of ferrocenes, which are characterized by two rotatory coplanar cyclopentadienyl (Cp) rings and redox properties, has been focused on in the development of molecular receptors.[1] Another interesting feature of ferrocenes is its inter-ring separation of ca. 3.3 Å, which is similar to the distance of the N···O hydrogen bond. In this respect, ferrocenes can be regarded as a molecular scaffold to study the hydrogen-bonding properties of peptide strands.[2] We have already demonstrated that the incorporation of the podand dipeptide chains -L-Ala-L-Pro-OR into ferrocene leads to an ordered structure through two rigid intramolecular interchain hydrogen bondings.[3] These intriguing results prompted us to investigate the effect of the kind and sequence of amino acids on the formation of an ordered structure. This paper describes the hydrogen-bonding properties of dipeptide chains of ferrocenes bearing podand dipeptide chains composed of glycine and L-proline to induce intramolecular conformational regulation.

Results and Discussion

Glycine and L-proline, which are the smallest amino acid and a well-known turn inducer to promote a β-turn or γ-turn in proteins, respectively,[4] were chosen to effect conformational regulation on the basis of the hydrogen bondings and the stereochemically constrained structure. The ferrocenes **1**−**4** were synthesized from the corresponding 1,1′-bis(chlorocarbonyl)ferrocene or (chlorocarbonyl)ferrocene and dipeptide ethyl ester hydrogen chloride (Figure 1) and were fully characterized by spectral data and elemental analyses.

X-ray crystallographic analyses were performed in order to clarify an intramolecular conformational control in the ferrocene **1** bearing the podand dipeptide chains -Gly-L-Pro-OEt (Tables 1−3). The numbering of selected atoms of **1** is shown in Figure 2. The crystal structure of **1** confirmed the formation of two intramolecular hydrogen bondings between CO (Gly) and NH (another Gly) of each podand dipeptide chain (N(1)···O(102), 2.910 Å; N(101)···O(2), 2.898 Å; N(201)···O(302), 2.85 Å; N(301)···O(202), 2.87 Å) to give a 10-membered hydrogen-bonded ring (Figure 3 and Table 2). In the asymmetric unit, there are two independent molecules with the almost same conformation. Although a wide

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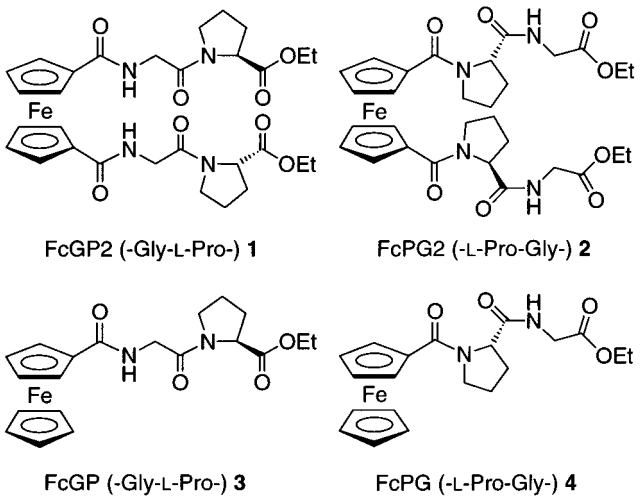

Figure 1. Ferrocenes bearing dipeptide chains.

Table 1. Crystallographic Data for 1 and 3

	1	3
formula	$C_{30.5}H_{38.5}N_4O_8FeCl_{1.5}$	$C_{20}H_{24}N_2O_4Fe$
fw	698.19	412.27
cryst syst	monoclinic	tetragonal
space group	$P2_1$ (No. 4)	$P4_3$ (No. 78)
a, Å	11.8903(4)	11.249(2)
b, Å	16.4379(7)	
c, Å	16.8729(5)	15.580(9)
β, deg	94.0894(9)	
Z	4	4
D_{calcd}, g cm^{-3}	1.410	1.389
μ(Mo Kα), cm^{-1}	6.34	7.91
T, °C	23	23
λ(Mo Kα), Å	0.710 69	0.710 69
R	0.047[a]	0.061[a]
R_w	0.130[b]	0.057[c]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2)^2]^{1/2}$. [c] $R_w = [\sum w(|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Hydrogen Bonds for 1 and 3

cryst	type[a]	donor	acceptor	D···A (Å)	D−H···A (deg)
1[b]	intra	N(1)	O(102)	2.910(4)	159(4)
	intra	N(101)	O(2)	2.898(5)	154(4)
	intra	N(201)	O(302)	2.85(1)	151(4)
	intra	N(301)	O(202)	2.87(1)	150(4)
3	inter	N(1)	O(2a)	2.88(1)	169(7)
	inter	N(1b)	O(2)	2.88(1)	169(7)

[a] Abbreviations: inter, intermolecular; intra, intramolecular. [b] Two independent molecules exist in the asymmetric unit.

range of relative orientations is possible depending on two rotatory Cp rings, the podand dipeptide chains are arrayed in the same direction through two intramolecular hydrogen bonds to induce an ordered structure. Two intramolecular hydrogen bonds require rotation of the peptide chains, resulting in the observed torsion angles ($\phi_1 = -82.2$ and $-82.1°$, $\psi_1 = 176.5$ and $-175.4°$, $\phi_1* = -98.9$ and $-83.5°$, $\psi_1* = -162.6$ and $-173.1°$) as listed in Table 3. The torsion angles ω_1 and ω_1* ($\omega_1 = -177.6$ and $175.4°$, $\omega_1* = -169.5$ and $179.9°$) indicate a nearly *trans* comformation of the Pro moiety.

In the ^{1}H NMR spectra of the ferrocene **1** in $CDCl_3$ (1.0×10^{-2} M), only one kind of N−H resonance was detected at a lower field (8.77 ppm) than that of the ferrocene **3** bearing one dipeptide chain (-Gly-L-Pro-OEt) (2.0×10^{-2} M, 6.69 ppm). The N−H resonance of **1** was not perturbed by the addition of aliquots of DMSO-d_6 to $CDCl_3$, although a slightly downfield shift was observed with **3** (Table 4). These results indicate that two identical intramolecular hydrogen bonds between the podand dipeptide chains of **1** are present in solution. The FT-IR spectrum of **1** in CH_2Cl_2 (1.0×10^{-2} M) showed only one N−H stretching band at 3316 cm^{-1}, which also supports the hydrogen bonding in **1**. The ferrocene **1** exhibited an induced circular dichroism (CD) around the absorbance of the ferrocene function, in sharp contrast to the finding that such induced CD was not detected in the case of **3**, which is not able to form an ordered structure via intramolecular hydrogen bonding (Figure 4). The ferrocene **1** is assumed to form an ordered structure on the basis of the formation of a 10-membered hydrogen-bonded ring even in solution, just as is observed in the crystal structure. In contrast, the ferrocene **3** formed a hydrogen-bonded network, in which each molecule is connected to two neighboring molecules through intermolecular hydrogen bonds between CO (Ala) and NH (another Ala) (N(1)···O(2a), 2.88 Å; N(1b)···O(2), 2.88 Å), instead of intramolecular hydrogen bonding (Figure 5a). It is noteworthy that the ferrocene **3** crystallizes in the $P4_3$ space group. The ferrocene **3** was found to be packed in a helically ordered arrangement with one turn of 15.65 Å pitch height through a network of intermolecular hydrogen bonds, within which the distance between the closest ferrocene units is 7.95 Å (Fe−Fe) as depicted in parts b and c of Figure 5.

To evaluate the effect of a sequence of amino acids on the intramolecular conformational regulation, the hydrogen-bonding properties of the ferrocene **2** bearing the podand dipeptide chains (-L-Pro-Gly-OEt) were examined next. The formation of an ordered structure in the ferrocene **2** was convincingly evidenced by observation of an intrinsic induced CD (Figure 6). The absence of an N−H bond in the proline unit is considered to lead to an intramolecular hydrogen bonding mode different from that of **1**. The ferrocene **2** exhibited only one kind of N−H resonance at 9.50 ppm in ^{1}H NMR and an amide N−H stretching band at 3267 cm^{-1} in FT-IR (Table 4), suggesting the presence of two identical hydrogen bonds. A proton magnetic resonance nuclear Overhauser effect (NOE) study supports the intramolecular hydrogen bonding between CO (bridging) and NH (another Gly), as shown in Figure 7. Irradiation of the N−H of Gly enhances the resonance of the Cp protons of the α-C and α′-C positions (3.1% and 3.1%), indicating proximity between the N−H of Gly and Cp rings. NOE between the Gly α-CH_2 and the Cp proton of the α-C position was also observed (3.4% and 2.2%, respectively). Irradiation of the Pro α-CH resulted in a strong NOE with the resonance of the Cp proton of the α′-C position (9.9%). To gain insight into the conformational regulation by the intervention of intramolecular interchain hydrogen bondings, the ferrocene **4** bearing one dipeptide chain -L-Pro-Gly-OEt was investigated. The ferrocene **4** exhibited a small broad stretching band at 3286 cm^{-1} in the IR spectrum, suggesting the formation of a small fraction of γ-turn conformation.[5] However, in sharp contrast to the ferrocene **2**, NOEs and induced CD signals could not be detected. With these results taken into consideration, the ferrocene **2**

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Table 3. Torsion Angles (deg) for 1 and 3

	angle[a]	1[b]		3
ϕ_1	C(6)−N(1)−C(7a)−C(8)	−82.2(6)	−82.1(6)	−99.2(10)
ψ_1	N(1)−C(7a)−C(8)−N(2)	176.5(4)	−175.4(5)	177.3(8)
ω_1	C(7a)−C(8)−N(2)−C(9a)	−177.6(4)	175.4(5)	−179.3(9)
ϕ_2	C(8)−N(2)−C(9a)−C(10)	−75.5(6)	−52.0(7)	−81(1)
ψ_2	N(2)−C(9a)−C(10)−O(4)	162.7(5)	134.8(5)	169.3(8)
ϕ_{1*}	C(106)−N(101)−C(107a)−C(108)	−98.9(7)	−83.5(6)	
ψ_{1*}	N(101)−C(107a)−C(108)−N(102)	−162.6(4)	−173.1(5)	
ω_{1*}	C(107a)−C(108)−N(102)−C(109a)	−169.5(5)	179.9(5)	
ϕ_{2*}	C(108)−N(102)−C(109a)−C(110)	−72.2(6)	−70.2(7)	
ψ_{2*}	N(102)−C(109a)−C(110)−N(104)	151.1(5)	162.9(5)	

[a] Symbol used for torsion angles in peptides (IUPAC-IUB Commission on Biochemical Nomenclature). [b] Two independent molecules exist in the asymmetric unit.

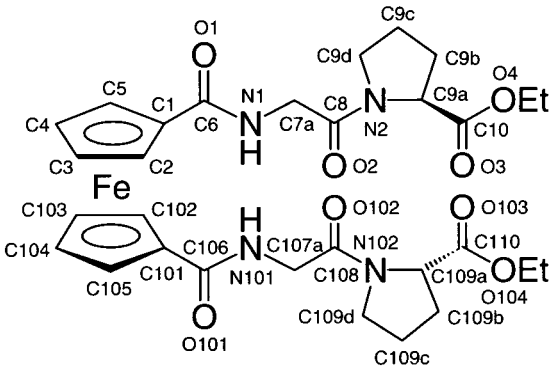

Figure 2. Numbering of selected atoms of the ferrocene **1**.

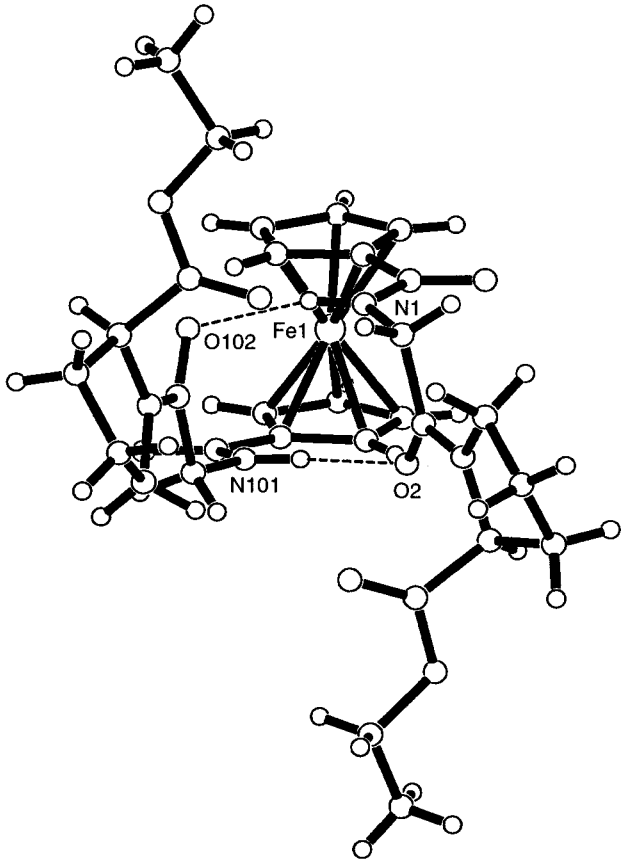

Figure 3. Molecular structure of **1**.

is assumed to form two rigid intramolecular hydrogen bondings between CO (bridging) and NH (another Gly) to construct an ordered structure with a 14-membered hydrogen-bonded ring as shown in Figure 7.

Table 4. Selected Spectroscopic Data for 1−4

	^{1}H NMR, N−H (ppm)[a]		FT-IR, ν_{N-H} (cm^{-1})[a]
	$CDCl_3$	$CDCl_3$/DMSO-d_6 (9:1)	CH_2Cl_2
1	8.77	8.72	3316
2	9.50	9.52	3267
3	6.69[b]	6.88[b]	3417[b]
4	7.48[b]	7.61[b]	3425[b], 3286[b]

[a] Concentration 1.0 × 10^{-2} M unless otherwise stated. [b] Concentration 2.0 × 10^{-2} M.

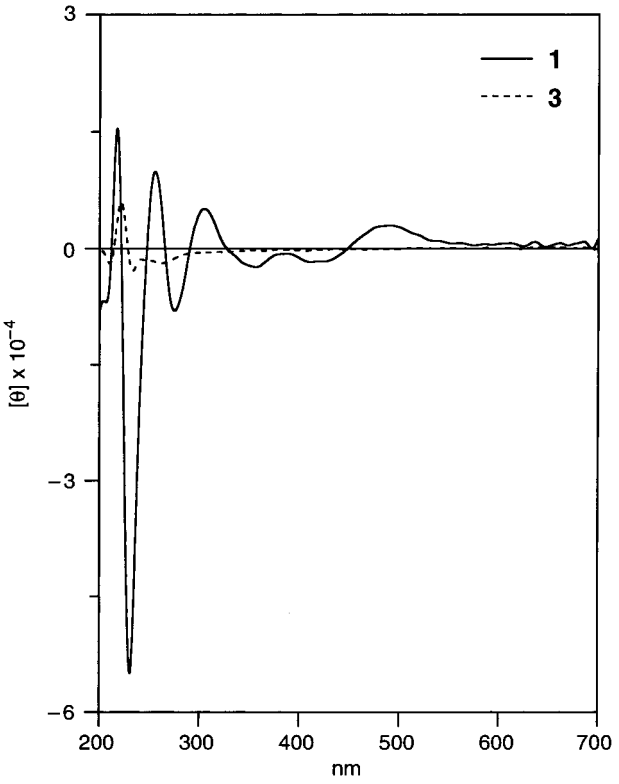

Figure 4. CD spectra of **1** and **3** in MeCN (1.0 × 10^{-4} M).

In conclusion, ferrocenes bearing podand dipeptide chains were demonstrated to induce intramolecular conformational regulation by intramolecular interchain hydrogen bonding. The ferrocene composed of the -Gly-L-Pro-OEt dipeptide chains formed a 10-membered hydrogen-bonded ring, although a 14-membered hydrogen-bonded ring was obtained with the -L-Pro-Gly-OEt dipeptide chains. The alternation of the sequence of amino acids resulted in a different intramolecular conformational regulation. The ferrocene scaffold allows the two dipeptide chains of each Cp ring in the same direction either by the free rotation of the Cp rings of

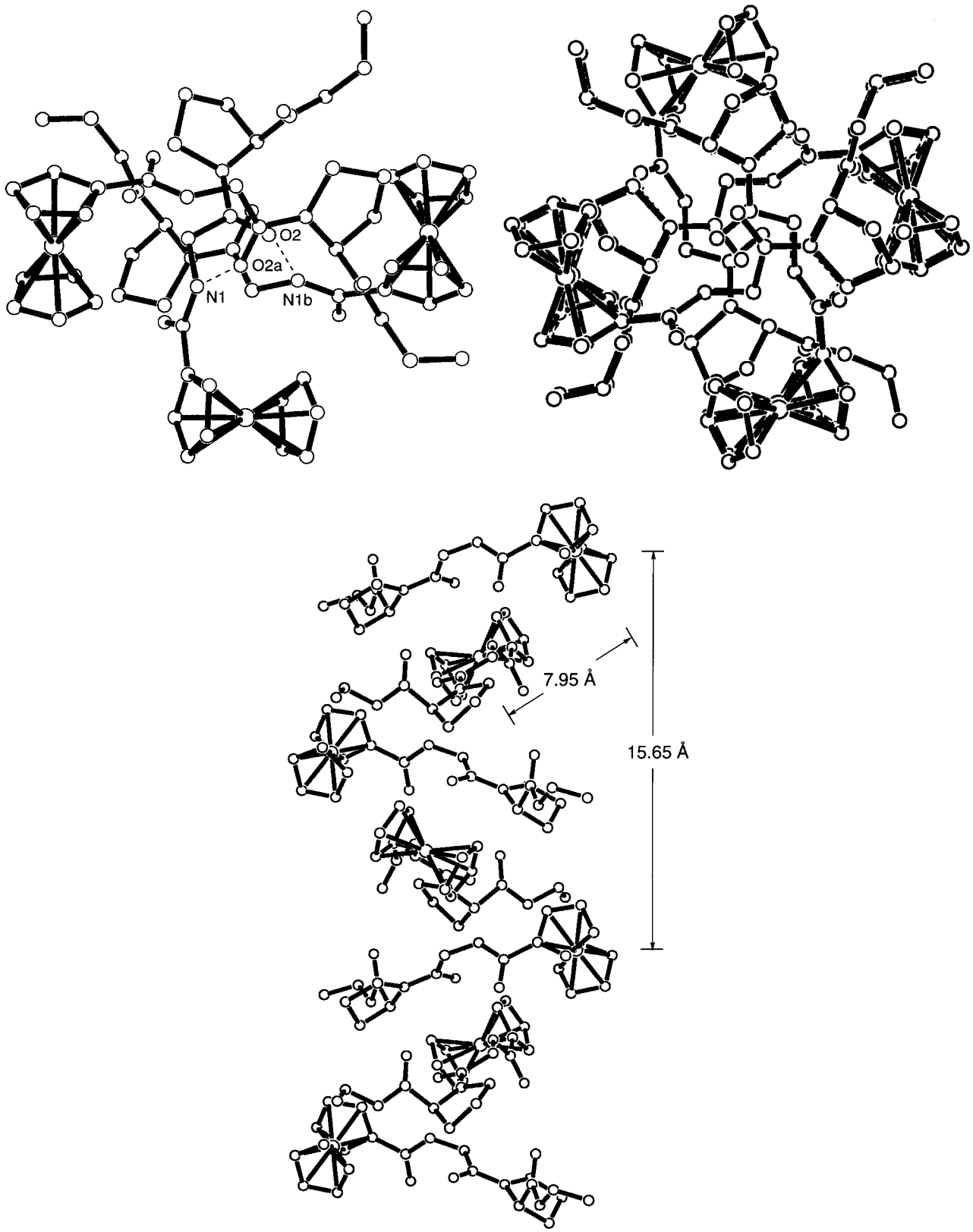

Figure 5. (a, top left) Hydrogen-bonded chain assembly of **3** in the crystal packing. Top view (b, top right) and side view (c, bottom) of a layer containing the helical arrangement of the crystal packing of **3**. The molecules are connected by continuous intermolecular hydrogen bonds.

the ferrocene or by inducing intramolecular hydrogen bonding. The intramolecular hydrogen bonding and stereochemically constrained proline unit are considered to be an essential factor to induce an ordered structure. Furthermore, a helically ordered molecular arrangement through a network of intermolecular hydrogen bonds was demonstrated in the crystal packing of the ferrocene composed of the single -Gly-L-Pro-OEt dipeptide chain. Architectural control of molecular assemblies utilizing hydrogen bonding as observed in biological systems is considered to be one of the most convenient approaches to highly ordered supramolecular systems.

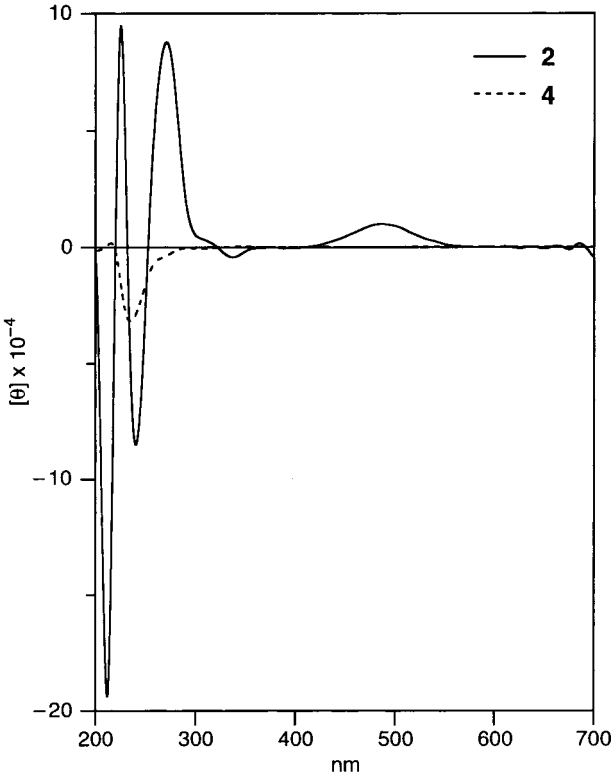

Figure 6. CD spectra of **2** and **4** in MeCN (1.0×10^{-4} M).

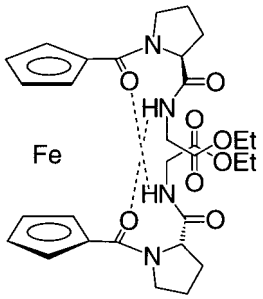

Figure 7. Proposed molecular structure of **2**.

Studies on molecular recognition based on the intramolecular conformational regulation of ferrocenes bearing podand dipeptide chains are now in progress.

Experimental Section

General Methods. All reagents and solvents were purchased from commercial sources and were further purified by standard methods, if necessary. 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 JEOL JNM-GSX-400 (400 MHz) spectrometer and a JEOL JNM-ECP 400 (400 MHz) instrument with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. Dipeptide ethyl ester hydrogen chlorides were prepared by esterification of the commercially available dipeptide with an alcohol under acidic conditions.

General Procedure for the Synthesis of Ferrocenes Bearing Podand Dipeptide Chains. To a stirred mixture of the dipeptide ethyl ester hydrogen chloride (0.60 mmol) and triethylamine (418 μL, 3.0 mmol) in dichloromethane (4 mL) was dropwise added 1,1′-bis(chlorocarbonyl)ferrocene (93.3 mg, 0.30 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 with dichloromethane as eluent. The ferrocene was isolated by recrystallization from dichloromethane−ethyl acetate.

1: yield 85%; mp 161−162 °C (uncorrected); IR (CH_2Cl_2, 1.0×10^{-2} M) 3316 (N−H), 1736 (C═O), 1643 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 1.0×10^{-2} M) δ 8.77 (dd, J = 5.1, 7.0 Hz, 2H), 5.06 (t, J = 1.5 Hz, 2H), 4.90 (t, J = 1.5 Hz, 2H), 4.57−4.46 (m, 6H), 4.29−4.27 (m, 2H), 4.22−4.10 (m, 4H), 3.77−3.65 (m, 4H), 3.58 (dd, J = 4.8, 16.4 Hz, 2H), 2.28−2.19 (m, 2H), 2.13−1.95 (m, 6H), 1.26 (t, J = 7.0 Hz, 6H); FAB-MS m/z 638 (M^+). Anal. Calcd for $C_{30}H_{38}N_4O_8Fe$: C, 56.43; H, 6.00; N, 8.77. Found: C, 56.45; H, 5.98; N, 8.85.

2: yield 72%; mp 175−176 °C (uncorrected); IR (CH_2Cl_2, 1.0×10^{-2} M) 3267 (N−H), 1747 (C═O), 1670 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 1.0×10^{-2} M) δ 9.50 (t, J = 5.5 Hz, 2H), 4.85 (br, 4H), 4.60 (d, J = 6.59 Hz, 2H), 4.38−4.09 (m, 12H), 3.80−3.61 (m, 4H), 2.49−2.44 (m, 2H), 2.03−1.87 (br, 6H), 1.30 (t, J = 7.6 Hz, 6H); FAB-MS m/z 638 (M^+). Anal. Calcd for $C_{30}H_{38}N_4O_8Fe$: C, 56.43; H, 6.00; N, 8.77. Found: C, 56.50; H, 6.07; N, 8.79.

General Procedure for the Synthesis of Ferrocenes Bearing One Dipeptide Chain. To a stirred mixture of the dipeptide ethyl ester hydrogen chloride (0.10 mmol) and triethylamine (70 μL, 0.50 mmol) in dichloromethane (2 mL) was dropwise added (chlorocarbonyl)ferrocene (24.9 mg, 0.10 mmol) in dichloromethane (3 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 $NaHCO_8$ 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 with dichloromethane as eluent.

3: yield 83%; mp 154−155 °C (uncorrected); IR (CH_2Cl_2, 2.0×10^{-2} M) 3417 (N−H), 1736 (C═O), 1643 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 2.0×10^{-2} M) δ 6.69 (br, 1H), 4.71 (t, J = 1.8 Hz, 2H), 4.56 (dd, J = 3.5, 4.3 Hz, 1H), 4.34 (t, J = 1.8 Hz, 2H), 4.30−4.08 (m, 9H), 3.70−3.52 (m, 2H), 2.33−1.90 (m, 4H), 1.29 (t, J = 7.0 Hz, 3H); FAB-MS m/z 412 (M^+). Anal. Calcd for $C_{20}H_{24}N_2O_4Fe$: C, 58.27; H, 5.87; N, 6.79. Found: C, 58.00; H, 5.83; N, 6.77.

4: yield 58%; viscous oil; IR (CH_2Cl_2, 2.0×10^{-2} M) 3425 (N−H), 3286 (N−H), 1743 (C═O), 1682 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 2.0×10^{-2} M) δ 7.48 (t, J = 5.3 Hz, 1H), 4.87−4.86 (m, 1H), 4.81 (dd, J = 3.7, 7.7 Hz, 1H), 4.77−4.76 (m, 1H), 4.43−4.40 (m, 2H), 4.26 (s, 5H), 4.20 (q, J = 7.1 Hz, 2H), 4.07 (dd, J = 1.8, 5.3 Hz, 2H), 3.86−3.83 (m, 2H), 2.45−2.36 (m, 1H), 2.25−2.14 (m, 1H), 2.08−1.96 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); FAB-MS m/z 412 (M^+). Anal. Calcd for $C_{20}H_{24}N_2O_4Fe$: C, 58.27; H, 5.87; N, 6.79. Found: C, 57.87; H, 5.90; N, 6.73.

Proton Magnetic Resonance Nuclear Overhauser Effect Measurements. A sample was prepared under a dry argon atmosphere. A nuclear Overhauser effect experiment was performed at 25 °C and 400 MHz with 2 s irradiation of a freeze−pump−thaw-degassed 10 mM sample in $CDCl_3$ solution. Nuclear Overhauser enhancements were obtained by saturation of the desired resonance.

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

X-ray Structure Analysis. All measurements for **1** were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All measurements for **3** were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a rotating anode generator. The structures of **1** and **3** were solved by

direct 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 1.

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Supporting Information Available: Tables of X-ray crystallographic data for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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