Journal of Organometallic Chemistry 694 (2009) 806–811

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Review

Control of chirality-organized structures of ferrocene–dipeptide bioconjugates

Toshikazu Hirao *

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

ARTICLE INFO

Article history:
Received 25 August 2008
Received in revised form 17 September 2008
Accepted 17 September 2008
Available online 30 October 2008

Keywords:
Bioorganometallic chemistry
Ferrocene
Dipeptide
Chirality organization
Secondary structure

ABSTRACT

A variety of ferrocene–dipeptide bioconjugates have been designed to induce chirality-organized structures in both solid and solution states. The ferrocene serves as a reliable organometallic scaffold for the construction of protein secondary structures via intramolecular hydrogen bonding, here the attached dipeptide strands are regulated within the appropriate dimensions. The configuration and sequence of the amino acids play an important role in the construction of the chirality-organized bio-inspired systems under controlled hydrogen bonding.

Contents

1. Introduction

Architectural control of molecular self-organization is achieved by constructing highly-ordered structures in proteins to fulfill unique functions, as observed for example, in enzymes and receptors. Secondary structures such as α-helices, β-sheets, and β-turns play an important role in protein folding, which is mostly stabilized by hydrogen bonding and hydrophobic interaction of the side chains [1]. Highly specific patterns of complementary intra- and intermolecular hydrogen bonds are created in such secondary structures. Although β-sheets are a key structural element in a three-dimensional structure, the structure and stability of the β-sheets are less understood compared to those of α-helices. Generally, preparation of chemical models of β-sheets is difficult due to the complexity of the folding and propensity for self-association. Additionally predicting the pattern of protein foldings from the sequence of amino acids is extremely challenging. The utilization of molecular scaffolds is a potential strategy for organization of peptide structures, which allows control of the intramolecular interaction between peptide or peptidomimetic strands. Therefore, various molecular scaffolds such as a rigid aromatic ring [2], an epindolidion [3], a dibenzofuran [4], an oligourea [5], and an *endo-cis*-(2*S*,3*R*)-norbornene [6] scaffold have been employed to create the β-sheet-like structures of attached peptide chains and serve as β-turn substitutes for the chemical models of protein secondary structures. In addition to organic molecular scaffolds, ferrocenes are recognized as organometallic scaffolds in a central reverse-turn unit based on the inter-ring spacing of ferrocene, (approximately 3.3 Å), which is suitable for hydrogen bonding of the attached peptide strands [7,8]. Another advantage in the use of ferrocene as a scaffold that it is dependent on the electrochemical reversibility of the redox couple, which permits the usage of a redox-switching center and an electrophore. Recent bioorganometallic research, a hybrid of biochemistry and organometallic chemistry, has drawn much attention. Conjugation of organometallic compounds with biomolecules such as DNA, amino acid, and peptide are foreseen to provide novel systems by

* Fax: +81 6 6879 7415.
E-mail address: hirao@chem.eng.osaka-u.ac.jp

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.09.074

combining the beneficial properties of each component. Considerable effort has been devoted to designing the bioconjugates [9]. We have already demonstrated that redox-active ferrocenes, bearing a long alkylene chain, are aggregated along the backbone of double helical DNA, presenting a redox-active (outer) and hydrophobic (inner) spheres around the double helical core [10]. The introduction of peptides into the ferrocene scaffold as a central reverse-turn unit has been investigated to obtain peptidomimetic basis for protein folding and to construct highly-ordered molecular assemblies [11]. In this paper, we summarize our ongoing research on the ferrocene–dipeptide bioconjugates [11a,11c,11i,11j].

2. Synthesis and chirality organization of ferrocene–peptide bioconjugates

Our design is based on a symmetrical introduction of two dipeptide chains of alanyl-proline or prolyl-alanine sequence (-Ala-Pro-) into the ferrocene scaffold as a central reverse-turn unit. An advantage in the use of the dipeptide chain depends on a hydrogen bonding site of alanine and a sterically constrained proline as a well-known turn inducer in proteins.

X-ray crystallographic analyses are performed to clarify ordered structures of the ferrocene–dipeptide bioconjugates. The incorporation of the dipeptide chains (-L-Ala-L-Pro-OEt) into the ferrocene scaffold, achieves the chirality-organized structure based on two rigid intramolecular hydrogen bonds, although a wide range of relative orientations are possible depending on two rotatory Cp rings. The single-crystal X-ray structure of the ferrocene–peptide bioconjugate **1** bearing -L-Ala-L-Pro-OEt reveals the intramolecular antiparallel β-sheet-like hydrogen bonding between NH (Ala) and CO (Ala of another chain) of each dipeptide chain (N(1)···O(2*), 3.000(6) Å; N(1*)···O(2), 3.000(6) Å) to induce the chirality-organized structure (Fig. 1a). The ferrocenyl moiety adopts the *P*-helical arrangement. The conformational enantiomers based on the torsional twist about the Cp(centroid)-Fe-Cp(centroid) axis are possible with the 1,1′-disubstituted ferrocene as shown in Fig. 2 [12]. To evaluate the ability of ferrocenes possessing dipeptide chains, inducing conformational enantiomerization, the crystal structure of **2** bearing the corresponding D-dipeptide chains (-D-Ala-D-Pro-OEt) is examined. The crystal structure of **2** reveals the formation of two C_2-symmetrical intramolecular hydrogen bondings between CO (Ala) and NH (another Ala) of each dipeptide chain

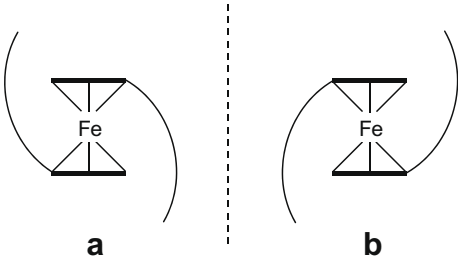

Fig. 2. Enantiomorphous conformations of the 1,1′-disubstituted ferrocene. The enantiomorphs are related by the mirror plane.

(N(1)···O(2*), 2.981(8) Å; N(1*)···O(2), 2.981(8) Å), in which the *M*-helical arrangement of the ferrocenyl moiety is formed (Fig. 1b). The molecular structures of **1** and **2** are in an excellent mirror image relationship as shown in Fig. 1, indicating conformational enantiomers present (Fig. 2). These results imply the introduction of the chiral dipeptide chains into the ferrocene scaffold induces the chiral molecular arrangement based on the ordered structure, via the intramolecular hydrogen bondings (Chart 1).

Circular dichroism (CD) spectrometry is a useful tool to determine an ordered structure in solution. The ferrocene–dipeptide bioconjugate **1** exhibits an induced circular dichroism (ICD) at the absorbance region of the ferrocenyl moiety in acetonitrile, which indicates the *P*-helical arrangement of the ferrocenyl moiety (Fig. 3). The mirror image of the signals is obtained in the CD spectrum of **2**, indicating the chiral molecular arrangement based on an ordered structure via intramolecular interchain hydrogen bonding is formed even in solution. Furthermore, two identical intramolecular hydrogen bonds between the dipeptide chains are supported by ^{1}H NMR ($CDCl_3$) and FT-IR (CH_2Cl_2) analyses.

3. Effect of configuration and sequence of dipeptide chains on chirality organization of ferrocene–peptide bioconjugates

Chirality choice and sequence of amino acids are considered a key factor for constructing chirality-organized bio-inspired systems with highly ordered structures. The effect of the configuration and sequence of the dipeptide chains on the organization of the template structure is examined. The single-crystal X-ray structure

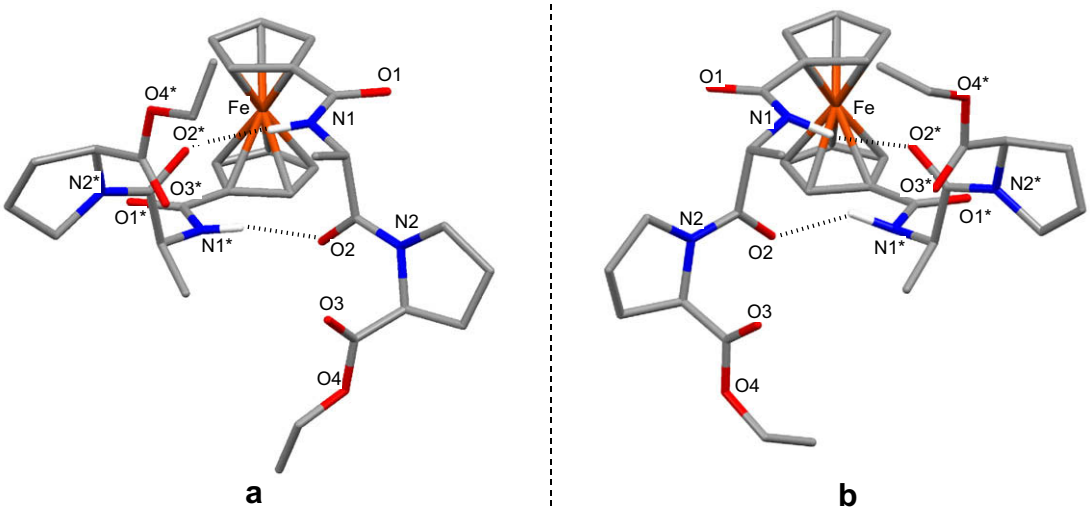

Fig. 1. Molecular structures of (a) **1** and (b) **2**.

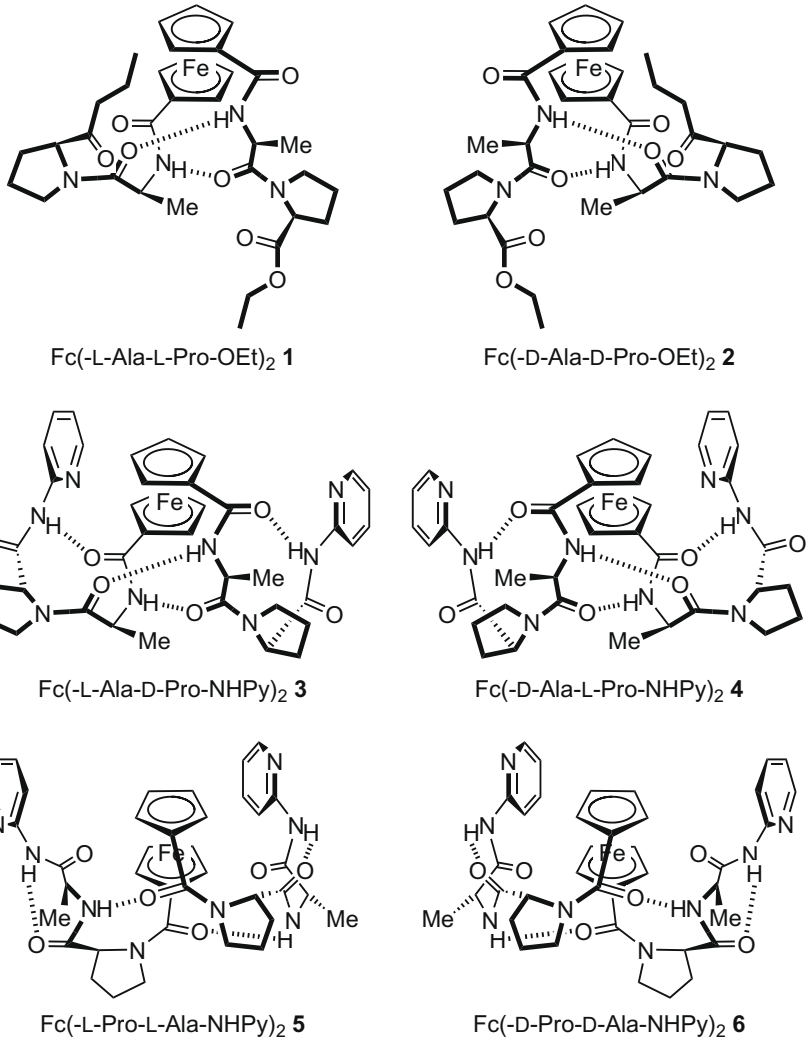

Chart 1. Ferrocene–dipeptide bioconjugates bearing the dipeptide chains.

determination of the ferrocene–dipeptide bioconjugate **3** bearing -L-Ala-D-Pro-NHPy reveals the intramolecular antiparallel β-sheet-like hydrogen bonding between NH (Ala) and CO (Ala of another chain) of each dipeptide chain (N(1)···O(2*), 3.069(7) Å; N(1*)···O(2), 2.973(7) Å) to induce the chirality-organized structure (Fig. 4a). The *P*-helical arrangement of the ferrocenyl moiety appears to be controlled by the configuration of the alanyl α-carbon atom, as a similar type of the chiral molecular conformation is also observed in the ferrocene–dipeptide bioconjugate **1** bearing -L-Ala-L-Pro-OEt. The helical chirality of the proposed ferrocenyl moiety is determined by the configuration of the amino acid adjacent to the ferrocenoyl moiety [7l,7n]. Conformational enantiomerization through chirality organization is achieved by restricting the torsional twist on the intramolecular hydrogen bonds and the chiral centers in the peptide chains. Another remarkable feature of the structure is that the NH, adjacent to the pyridyl moiety, participates in the intramolecular hydrogen bonding, with the CO adjacent to the ferrocene unit of the same peptide chain (N(3)···O(1), 3.223(7) Å; N(3*)···O(1*), 3.153(7) Å), to nucleate a β-turn-like structure in each dipeptide chain. The torsion angles φ_2 ($\varphi_2 = -64.5°$ and $\phi_2^* = -63.8°$), ψ_2 ($\psi_2 = 134.0°$ and $\psi_2^* = 136.0°$), φ_3 ($\varphi_3 = 68.7°$ and $\phi_2^* = 75.1°$), and ψ_3 ($\psi_3 = 19.2°$ and $\phi_3^* = 9°$) of **3** indicate a type II β-turn-like structure despite $\varphi_2 = -60°$, $\psi_2 = 120°$, $\varphi_3 = 80°$, and $\psi_3 = 0°$ for an ideal type II β-turn. The combination of the ferrocene scaffold as a central reverse-turn unit with the -L-alanyl-D-proline hetrochiral sequence as a dipeptide unit permits the artificially regulated antiparallel β-sheet-like and type II β-turn-like structures simultaneously. The molecular structure of **4** composed of the dipeptide chains (-D-Ala-L-Pro-NHPy), in which the *M* helical arrangement of the ferrocenyl moiety is formed (Fig. 4b), is in an excellent mirror image relationship with **3**, indicating **3** and **4** are conformational enantiomers (Fig. 4). The opposite values of the torsion angles of **4** (φ_2 ($\varphi_2 = 65.0°$ and $\phi_2^* = 64.0°$), ψ_2 ($\psi_2 = -134.7°$ and $\phi_2^* = -136.3°$), φ_3 ($\varphi_3 = -67.5°$ and $\phi_3^* = -74.7°$), and ψ_3 ($\psi_3 = -18.7°$ and $\phi_3^* = -10.5°$)) are observed compared with **3**.

An ICD, at the absorbance region of the ferrocenyl moiety, is detected in a CD spectrum of the ferrocene–peptide bioconjugate **3** in dichloromethane, indicating the *P*-helical arrangement of the ferrocenyl moiety (Fig. 5). The mirror-imaged CD signals are obtained in the case of **4**. The chiral molecular arrangements based on an ordered structure via intramolecular interchain hydrogen bondings are likely to be present, even in solution. Proton magnetic resonance Nuclear Overhauser Effect (NOE) of **3** in $CDCl_3$ at 25 °C additionally provides diagnostic evidence for this structure. Irradiation of the Cp proton at the β position enhances the pyridyl protons. Irradiation of the Cp proton at the α position also enhances the Ala NH, NH adjacent to the pyridyl moiety, and pyridyl proton at the 3-position. A type II β-turn-like structure is achieved in solution.

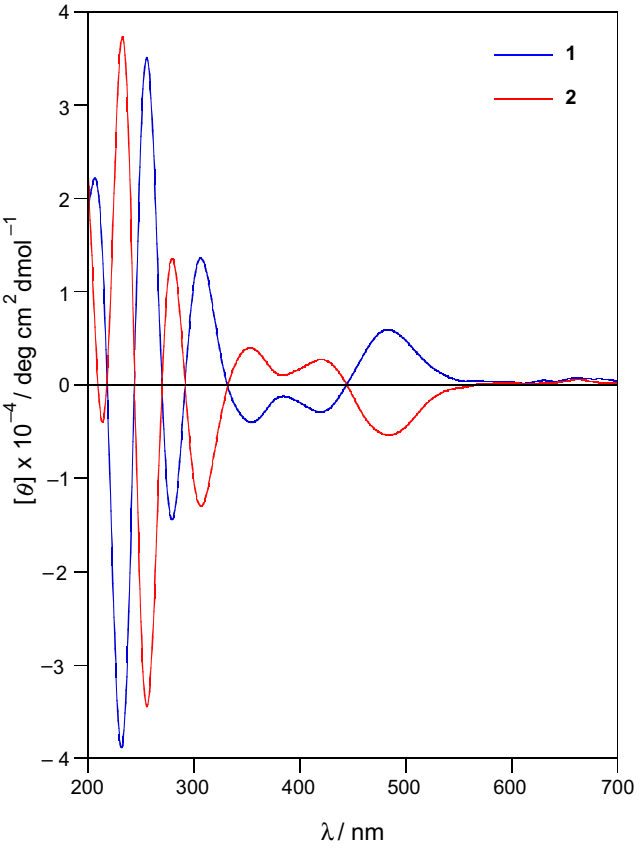

Fig. 3. CD spectra of **1** and **2** in acetonitrile (1.0×10^{-4} M).

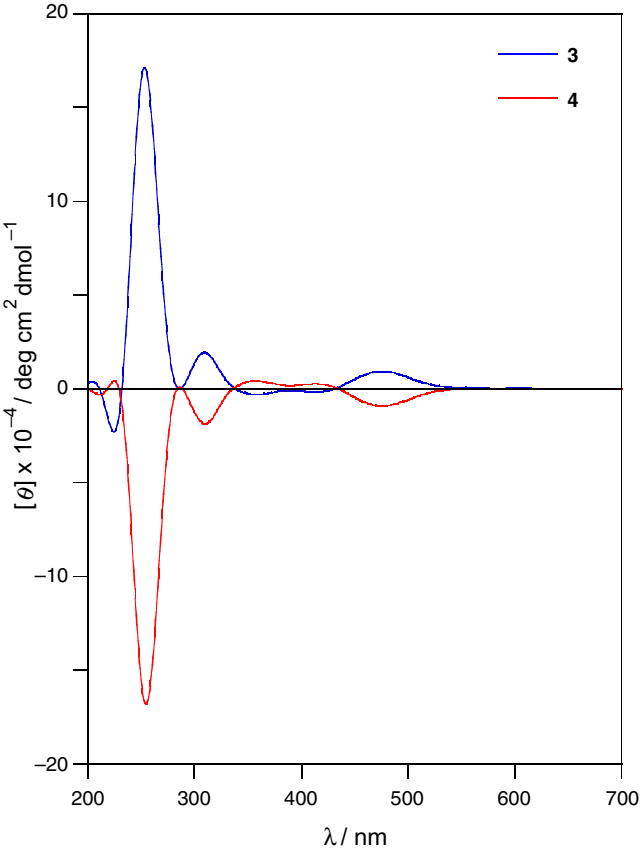

Fig. 5. CD spectra of **3** and **4** in dichloromethane (1.0×10^{-4} M).

The crystal structure of the ferrocene–peptide bioconjugate **5** bearing -L-Pro-L-Ala-NHPy is characterized by the presence of the NH adjacent to the pyridyl moiety participating in an intramolecular hydrogen bond with the Pro CO of the same peptide chain (N(3)···O(2), 3.032(4) Å; N(3*)···O(2*), 2.996(4) Å). Nucleating a γ-turn-like structure in each dipeptide chain, where the interchain intramolecular antiparallel β-sheet-like hydrogen bondings between the NH of the Ala and the CO of the ferrocene unit attached to the opposite peptide chain (N(2)···O(1*), 2.978(2) Å; N(2*)···O(1), 2.836(3) Å) are formed (Fig. 6a). The torsion angles φ_2 ($\varphi_2 = -90.5°$ and $\phi_2^* = -89.5°$) and ψ_2 ($\psi_2 = 60.9°$ and $\phi_2^* = 58.4°$) of **5** indicate an inverse γ-turn-like structure similar to an ideal inverse γ-turn ($\varphi_2 = -70°$ to $-85°$ and $\psi_2 = 60°$–$70°$). The combination of the ferrocene scaffold with the L-prolyl-L-alanine homochiral sequence permits the simultaneous formation of the artificial inverse γ-turn-like and antiparallel β-sheet-like structures. The molecular structure of **6** composed of the D-Pro-D-Ala-NHPy dipeptide chains (Fig. 6b) is in a mirror image relationship with **5**, indicating that **5** and **6** are the conformational isomers (Fig. 6). The opposite values of the torsion angles of **6** ($\varphi_2 = 90.6°$, $\phi_2^* = 89.4°$, $\psi_2 = -60.7°$, and $\phi_2^* = -57.9°$) compared with **5** are in direct agreement with the conformational isomers. The ferrocenyl moiety is restricted around the Cp(centroid)-Fe-Cp(centroid) axis and the C(*ipso*)–CO bond due to the intramolecular hydrogen bonds between the dipeptide chains.

The ferrocene–dipeptide bioconjugate **5** exhibits an ICD at the absorbance region of the ferrocene moiety based on the chirality-organized structure, being in a mirror image relationship with **6** (Fig. 7). Enhancement of the pyridyl protons by Cp proton irradiation at the β position is observed in NOE measurement of **5** in

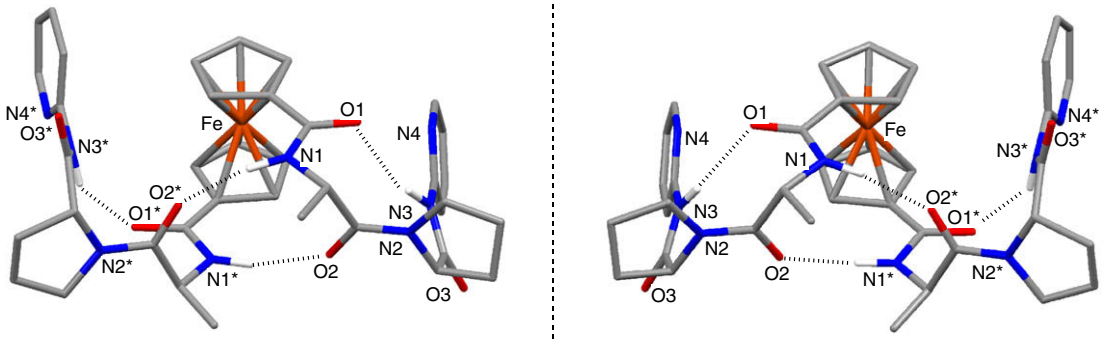

Fig. 4. Molecular structures of (a) **3** and (b) **4**.

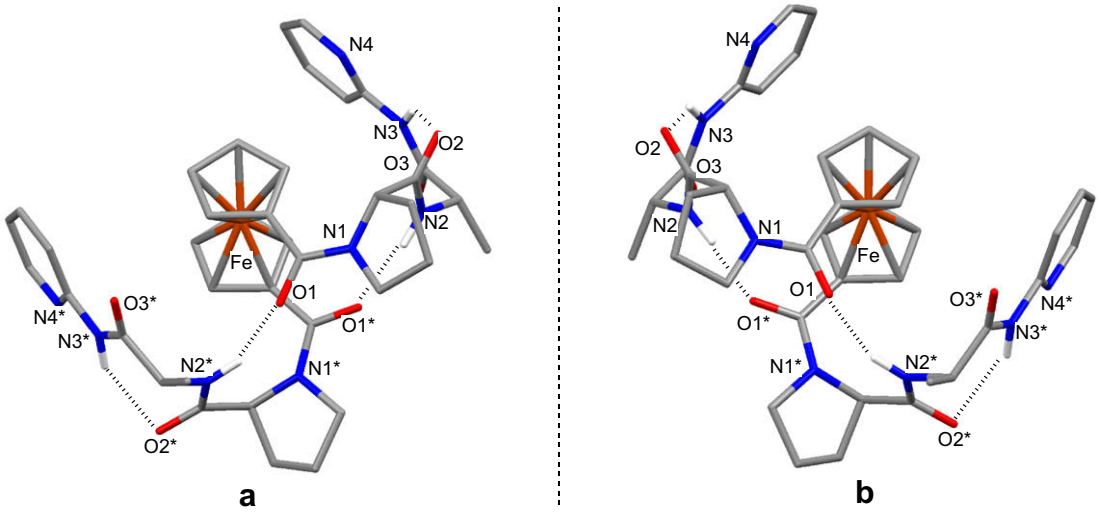

Fig. 6. Molecular structures of (a) **5** and (b) **6**.

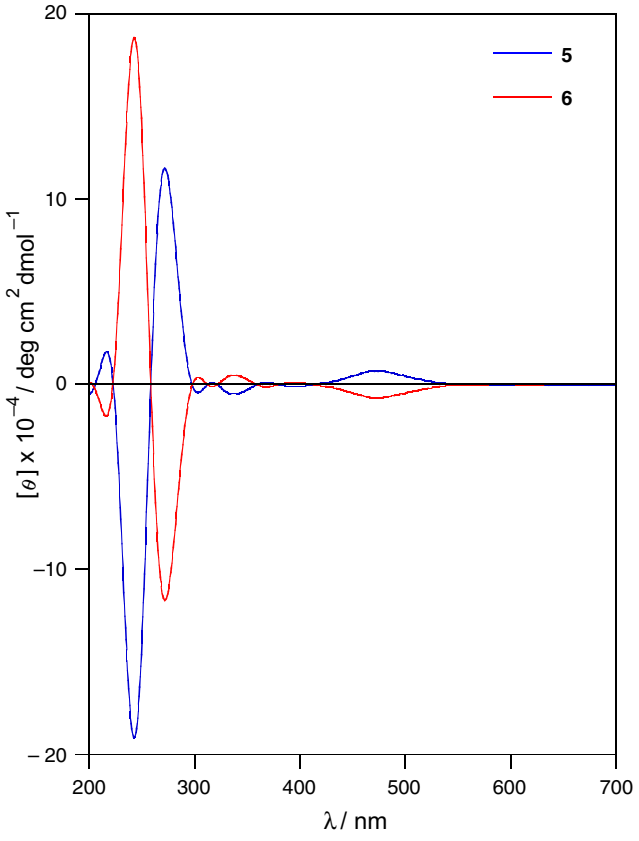

Fig. 7. CD spectra of **5** and **6** in dichloromethane (1.0×10^{-4} M).

$CDCl_3$ at 25 °C. Irradiation of the Cp proton at the α position also enhances the Ala NH, NH adjacent to the pyridyl moiety, Pro α-CH, and pyridyl proton at the 3-position. These results support the formation of an inverse γ-turn-like structure even in solution. Compared with the ferrocene–peptide bioconjugates bearing the -Ala-Pro-NHPy chains ($E_{1/2}$: **3**, 0.28 V; **4**, 0.28 V versus Fc/Fc^+), the ferrocene–peptide conjugates **5** and **6** exhibit a reversible Fc/Fc^+ redox wave at a more positive value ($E_{1/2}$: **5**, 0.35 V; **6**, 0.35 V versus Fc/Fc^+), likely due to the absence of NH in the Pro moieties.

4. Conclusion

A variety of ferrocene–peptide bioconjugates have been designed to induce highly ordered structures of peptides. The ferrocene serves as a reliable organometallic scaffold for the construction of the chirality-organized structure via intramolecular hydrogen bondings, here the attached dipeptide strands are regulated within the appropriate dimensions. Conformational enantiomerization, through chirality organization, is achieved by restricting the torsional twist around the Cp(centroid)-Fe-Cp(centroid) axis and the C(*ipso*)–CO bond through the intramolecular hydrogen bonds between the dipeptide chains. The configuration and sequence of the amino acids are found to play an important role in the construction of the chirality-organized bio-inspired systems under controlled hydrogen bonds. The combination of the ferrocene scaffold, as a central reverse-turn unit, with the -L-alanyl-D-proline hetrochiral sequence, as a dipeptide unit, induces the antiparallel β-sheet-like and type II β-turn-like structures simultaneously. On the contrary, the combination with the -L-prolyl-L-alanine homochiral sequence as a dipeptide unit is found to induce the simultaneous formation of the inverse γ-turn-like and antiparallel β-sheet-like structures. These chemical models of the protein secondary structures afford fundamental insight into the factors affecting protein structure and stability. The architectural control of molecular assemblies utilizing dipeptide chains, which possess chiral centers and hydrogen bonding sites, is envisioned to be a useful approach to artificial highly-ordered systems. This bioorganometallic chemistry is predicted to provide not only a peptidomimetic basis for protein folding, but also pharmacologically useful compounds, artificial receptors, asymmetric catalysts, and new materials with functional properties.

Acknowledgements

I express my gratitude to Dr. T. Moriuchi, Dr. A. Nomoto, K. Yoshida, and T. Nagai who significantly contributed to making this publication possible.

References

[1] (a) J. Kyte, Structure in Protein Chemistry, Garland, New York, 1995;
(b) C. Branden, J. Tooze, Introduction to Protein Structure, second ed., Garland, New York, 1998.

[2] (a) M. Feigel, J. Am. Chem. Soc. 108 (1986) 81;
(b) V. Brandmeier, M. Feigel, M. Bremer, Angew. Chem., Int. Ed. Engl. 28 (1989) 486;
(c) V. Brandmeier, M. Feigel, Tetrahedron 45 (1989) 1365;
(d) V. Brandmeier, W.H.B. Sauer, M. Feigel, Helv. Chim. Acta 77 (1994) 70.
[3] (a) D.S. Kemp, B.R. Bowen, Tetrahedron Lett. 29 (1988) 5077;
(b) D.S. Kemp, B.R. Bowen, Tetrahedron Lett. 29 (1988) 5081;
(c) D.S. Kemp, Trends Biotechnol. 8 (1990) 249;
(d) D.S. Kemp, C.C. Muendel, D.E. Blanchard, B.R. Bowen, in: J.E. Rivier, G.R. Marshall (Eds.), Peptides: Chemistry, Structure and Biology: Proceedings of the Eleventh American Peptide Symposium, ESCOM, Leiden, 1990, p. 674;
(e) D.S. Kemp, B.R. Bowen, C.C. Muendel, J. Org. Chem. 55 (1990) 4650.
[4] (a) H. Díaz, J.W. Kelly, Tetrahedron Lett. 32 (1991) 5725;
(b) H. Díaz, J.R. Espina, J.W. Kelly, J. Am. Chem. Soc. 114 (1992) 8316;
(c) H. Díaz, K.Y. Tsang, D. Choo, J.R. Espina, J.W. Kelly, J. Am. Chem. Soc. 115 (1993) 3790;
(d) H. Díaz, K.Y. Tsang, D. Choo, J.W. Kelly, Tetrahedron 49 (1993) 3533;
(e) N.R. Graciani, K.Y. Tsang, S.L. McCutchen, J.W. Kelly, Biorg. Med. Chem. 2 (1994) 999;
(f) K.Y. Tsang, H. Díaz, N. Graciani, J.W. Kelly, J. Am. Chem. Soc. 116 (1994) 3988.
[5] (a) J.S. Nowick, N.A. Powell, E.J. Martinez, E.M. Smith, G. Noronha, J. Org. Chem. 57 (1992) 3763;
(b) J.S. Nowick, M. Abdi, K.A. Bellamo, J.A. Love, E.J. Martinez, G. Noronha, E.M. Smith, J.W. Ziller, J. Am. Chem. Soc. 117 (1995) 89;
(c) J.S. Nowick, E.M. Smith, G. Noronha, J. Org. Chem. 60 (1995) 7386;
(d) J.S. Nowick, S. Mahrus, E.M. Smith, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 1066;
(e) J.S. Nowick, D.L. Holmes, G. Mackin, G. Noronha, A.J. Shaka, E.M. Smith, J. Am. Chem. Soc. 118 (1996) 2764;
(f) J.S. Nowick, E.M. Smith, M. Pairish, Chem. Soc. Rev. 25 (1996) 401;
(g) J.S. Nowick, M. Pairish, I.Q. Lee, D.L. Holmes, J.W. Ziller, J. Am. Chem. Soc. 119 (1997) 5413;
(h) J.S. Nowick, Acc. Chem. Res. 32 (1999) 287;
(i) J.S. Nowick, J.H. Tsai, Q.-C.D. Bui, S. Maitra, J. Am. Chem. Soc. 121 (1999) 8409;
(j) T. Moriuchi, T. Tamura, T. Hirao, J. Am. Chem. Soc. 124 (2002) 9356.
[6] (a) I.G. Jones, W. Jones, M. North, J. Org. Chem. 63: (1998) 1505;
(b) D. Ranganathan, V. Haridas, S. Kurur, A. Thomas, K.P. Madhusudanan, R. Nagaraj, A.C. Kunwar, A.V.S. Sarma, I.L. Karle, J. Am. Chem. Soc. 120 (1998) 8448;
(c) C.P.R. Hackenberger, I. Schiffers, J. Runsink, C. Bolm, J. Org. Chem. 69 (7) (2004) 39.
[7] (a) 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;
(b) T. Okamura, K. Sakauye, N. Ueyama, A. Nakamura, Inorg. Chem. 37 (1998) 6731;
(c) J.F. Gallagher, P.T.M. Kenny, M.J. Sheehy, Inorg. Chem. Commun. 2 (1999) 200;
(d) W. Bauer, K. Polborn, W. Beck, J. Organomet. Chem. 579 (1999) 269;
(e) H.-B. Kraatz, D.M. Leek, A. Houmam, G.D. Enright, J. Lusztyk, D.D.M. Wayner, J. Organomet. Chem. 589 (1999) 38;
(f) I. Bediako-Amoa, R. Silerova, H.-B. Kraatz, Chem. Commun. (2002) 2430;
(g) S. Maricic, U. Berg, T. Frejd, Tetrahedron 58 (2002) 3085;
(h) D.R. van Staveren, T. Weyhermüller, N. Metzler-Nolte, Dalton Trans. (2003) 210;
(i) T. Morita, S. Kimura, J. Am. Chem. Soc. 125 (2003) 8732;
(j) L. Barišić, M. Dropučić, V. Rapić, H. Pritzkow, S.I. Kirin, N. Metzler-Nolte, Chem. Commun. (2004) 2004;
(k) K. Heinze, M. Schlenker, Eur. J. Inorg. Chem. (2004) 2974;
(l) S.I. Kirin, D. Wissenbach, N. Metzler-Nolte, New J. Chem. 29 (2005) 1168;
(m) S. Chowdhury, K.A. Mahmoud, G. Schatte, H.-B. Kraatz, Org. Biomol. Chem. 3 (2005) 3018;
(n) K. Heinze, M. Beckmann, Eur. J. Inorg. Chem. (2005) 3450;
(o) S. Chowdhury, D.A.R. Sanders, G. Schatte, H.-B. Kraatz, Angew. Chem., Int. Ed. 45 (2006) 751;
(p) L. Barišić, M. Čakić, K.A. Mahmoud, Y.-n. Liu, H.-B. Kraatz, H. Pritzkow, S.I. Kirin, N. Metzler-Nolte, V. Rapić, Chem. Eur. J. 12 (2006) 4965;
(q) S. Chowdhury, G. Schatte, H.-B. Kraatz, Angew. Chem., Int. Ed. 45 (2006) 6882;
(r) K.A. Mahmoud, H.-B. Kraatz, Chem. Eur. J. 13 (2007) 5885;
(s) X. de Hatten, Z. Cournia, I. Huc, J.C. Smith, N. Metzler-Nolte, Chem. Eur. J. 13 (2007) 8139;
(t) S. Chowdhury, G. Schatte, H.-B. Kraatz, Angew. Chem., Int. Ed. 47 (2008) 6882.
[8] (a) T. Moriuchi, T. Hirao, Chem. Soc. Rev. 33 (2004) 294;
(b) D.R. van Staveren, N. Metzler-Nolte, Chem. Rev. 104 (2004) 5931;
(c) S.I. Kirin, H.-B. Kraatz, N. Metzler-Nolte, Chem. Soc. Rev. 35 (2006) 348;
(d) T. Moriuchi, T. Hirao, Ferrocene–peptide bioconjugates, in: G. Simonneaux (Ed.), Bioorganometallic Chemistry, vol. 17, Springer-Verlag, Berlin, Heidelberg, 2006, pp. 143–175;
(e) M. Salmain, N. Metzler-Nolte, Bioorganometallic chemistry of ferrocene, in: P. Stepnicka (Ed.), Ferrocenes, John Wiley & Sons, Chichester, 2008, pp. 499–639.
[9] (a) G. Jaouen, A. Vessiéres, I.S. Butler, Acc. Chem. Res. 26 (1993) 361;
(b) R. Severin, R. Bergs, W. Beck, Angew. Chem., Int. Ed. 37 (1998) 1634;
(c) G. Jaouen, J. Organomet. Chem., Bioorganomet. Chem. 589 (1999) 1–126.
[10] T. Hirao, A. Nomoto, S. Yamazaki, A. Ogawa, T. Moriuchi, Tetrahedron Lett. 39 (1998) 4295.
[11] (a) A. Nomoto, T. Moriuchi, S. Yamazaki, A. Ogawa, T. Hirao, Chem. Commun. (1998) 1963;
(b) T. Moriuchi, A. Nomoto, K. Yoshida, T. Hirao, J. Organomet. Chem. 589 (1999) 50;
(c) T. Moriuchi, A. Nomoto, K. Yoshida, A. Ogawa, T. Hirao, J. Am. Chem. Soc. 123 (2001) 68;
(d) T. Moriuchi, A. Nomoto, K. Yoshida, T. Hirao, Organometallics 20 (2001) 1008;
(e) T. Moriuchi, K. Yoshida, T. Hirao, Organometallics 20 (2001) 3101;
(f) T. Moriuchi, K. Yoshida, T. Hirao, J. Organomet. Chem. 637–639 (2001) 75;
(g) T. Moriuchi, K. Yoshida, T. Hirao, J. Organomet. Chem. 668 (2003) 31;
(h) T. Moriuchi, K. Yoshida, T. Hirao, Org. Lett. 5 (2003) 4285;
(i) T. Moriuchi, T. Nagai, T. Hirao, Org. Lett. 7 (2005) 5265;
(j) T. Moriuchi, T. Nagai, T. Hirao, Org. Lett. 8 (2006) 31;
(k) T. Moriuchi, T. Fujiwara, T. Hirao, J. Organomet. Chem. 692 (2007) 1353.
[12] (a) G. Cerichelli, B. Floris, G. Ortaggi, J. Organomet. Chem. 76 (1974) 73;
(b) A. Togni, T. Hayashi, Ferrocenes, VCH, Weinheim, 1995.