Electronic Supplementary Information

Dinuclear metal complexes composed of peptide chains: Solvent-induced switching and inversion of the metal-centered chirality

Naoki Ousaka, Yuki Takeyama, and Eiji Yashima*

Department of Molecular Design and Engineering, Graduate School of Engineering,

Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan.

*To whom correspondence should be addressed. E-mail:

yashima@apchem.nagoya-u.ac.jp

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Experimental Section

1. Instruments

The NMR spectra were taken using a Varian UNITY INOVA 500AS spectrometer. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS) as the internal standard in $CDCl_3$, and from a residual undeuterated solvent as the internal standard in DMSO-d_6 and CD_3CN. The DOSY experiments were carried out by using pulsed field gradient with the BPPSTE pulse sequence.[S1] The hydrodynamic diameters (d_h) were calculated from the diffusion constants (D) obtained by DOSY measurements according to the Einstein-Stokes equation, $d_h = k_B T/3\pi\eta_0 D$ (k_B: Boltzmann constant; T: absolute temperature; η_0: solvent viscosity; D: diffusion constant). The electron- and cold-spray ionization mass spectra (ESI-MS and CSI-MS) were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan) and a Bruker Daltonics microTOF-Q II spectrometer (Billerica, MA), respectively. The matrix-assisted laser desorption-ionization time-of-flight mass spectra (MALDI-TOF-MS) were measured using a Shimadzu AXIMA-CFR Plus spectrometer (Kyoto, Japan) with a positive mode using 1,8,9-anthracene triol (dithranol) as the matrix. The absorption and CD spectra were measured in 0.05-, 1-, and 3-cm quartz cells on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus (25 to 60 °C).

2. Materials

All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), Kokusan Chemical Co. Ltd., and Tokyo Kasei Kogyo (TCI) (Tokyo, Japan) unless otherwise noted. 2,2'-Bipyridiene-5-carboxylic acid was synthesized according to reference.[S2] All solvents [spectral quality grade (Wako Pure Chemical Industries)] for the preparation of Fe^{II} complexes were deoxygenated by bubbling argon gas prior to use.

3. Synthetic Procedures for the Ligand Peptides

Abbreviation of chemicals:

Z = benzyloxycarbonyl

Boc= *tert*-butoxycarbonyl

HATU = *O*-(7-azabenzotrizol-1-yl)-1,1,3,3- tetramethyluronium hexafluorophosphate

EDC = 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride

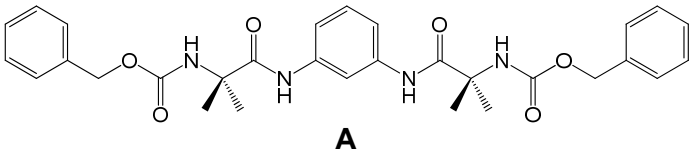
HOAt = 7-aza-1-hydroxy-1,2,3-benzotriazole

HOBt = 1-hydroxybenzotriazole monohydrate

DIEA = *N*,*N*-diisopropylethylamine

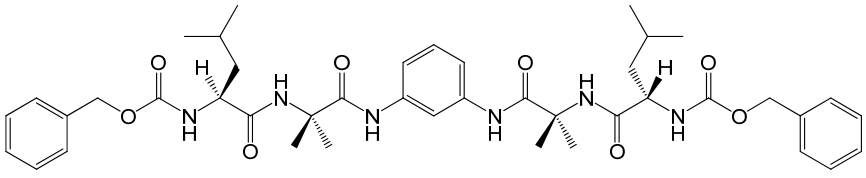
NMM = *N*-methylmorphorine

General Procedure for the Peptide Synthsis. Boc- and Z-protecting groups were removed by treatment with 4 N solution of HCl in 1,4-dioxane and with 10 % Pd-C/H_2 in MeOH, respectively. The resulting N-deprotected peptide hydrochloride salts and N-deprotected peptides were used without further purification. Peptide coupling reactions were carried out by HOAt/HATU or HOBt/EDC methods. 2,2'-Bipyridine-5-carbonyl chloride was prepared by heating the corresponding carboxylic acid with thionyl chloride at reflux for overnight.



A

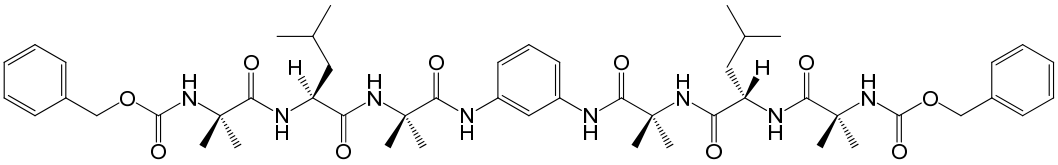
Peptide A. To a solution of Z-Aib-OH (3.00 g, 12.6 mmol) in dry CH_2Cl_2 (50 mL) were added HOAt (0.86 g, 6.32 mmol), HATU (4.81 g, 12.6 mmol), and DIEA (5.77 mL, 34.8 mmol) at 0 °C. After 20 min, to this was added *m*-phenylenediammonium dichloride (1.04 g, 5.75 mmol). The reaction mixture was stirred at 0 °C for 1 h and further at room temperature for 21 h. Then, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Recrystallization from $CHCl_3$/MeOH/*n*-hexane (ca. 5/1/5, v/v/v) afforded the peptide **A** (2.53 g, 80.5 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 569.24): found. 569.12. ^1H NMR (500 MHz, DMSO-d_6): δ = 9.45 (s, 2H), 7.96 (t, J = 1.9 Hz, 1H), 7.40 (s, 2H), 7.36-7.28 (bs + m, 12H), 7.18 (t, J = 8.1 Hz, 1H), 5.02 (s, 4H), 1.44 (s, 12H).



B

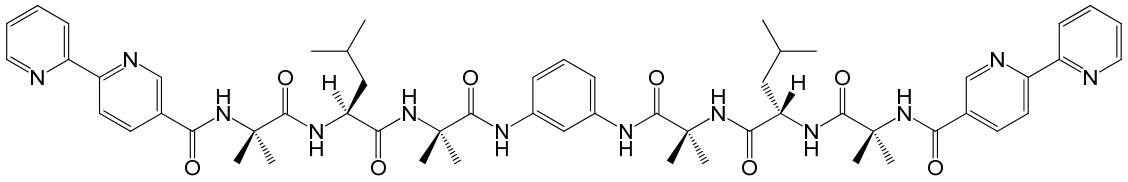
Peptide B. To a solution of Z-L-Leu-OH (820 mg, 3.09 mmol), HOBt (615 mg, 4.01 mmol), and N-deprotected peptide **A** (371 mg, 1.33 mmol) in DMF (4 mL) was added EDC (590 mg, 3.07 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h and further at room temperature for 15 h. Then, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Purification of the residue by column chromatography on silica gel (EtOAc as eluent) and further reprecipitation from EtOAc to Et_2O afforded peptide **B** (397 mg, 38.6 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 795.41): found. 795.44. ^1H NMR (500

MHz, $CDCl_3$): δ = 8.68 (s, 2H), 7.96 (s, 1H), 7.36-7.27 (m+m+s, 12H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.43 (s, 1H), 5.16-5.08 (dd+bs, *J* = 12.1, 17.3 Hz, 6H), 4.04-4.00 (m, 2H), 1.68-1.61 (m, 4H), 1.53-1.49 (bs+m, 14H), 0.95 (d, *J* = 6.2 Hz, 6H), 0.93 (d, *J* = 5.9 Hz, 6H).



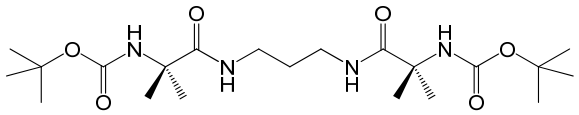
C

Peptide C. To a solution of Z-Aib-OH (348 mg, 1.41 mmol), HOBt (270 mg, 1.76 mmol), and N-deprotected peptide **B** (245 mg, 0.485 mmol) in DMF (3 mL) was added EDC (281 mg, 1.47 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and further at room temperature for 2 days. Then, the solution was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Purification of the residue by column chromatography on silica gel [$CHCl_3$/MeOH (9/1, v/v) as eluent] and further reprecipitation from CH_2Cl_2 to *n*-hexane afforded peptide **C** (302 mg, 65.0 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 965.51): found. 965.57. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.72 (s, 2H), 8.00 (s, 1H), 7.47 (bd, *J* = 7.8 Hz, 2H), 7.33-7.25 (m, 10H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.10 (s, 2H), 6.45 (d, *J* = 5.7Hz, 2H), 5.06-4.97 (dd, *J* = 12.2, 23.7 Hz, 4H), 4.17-4.13 (m, 2H), 1.76-1.45 (m+s+s+s+s, 30H), 0.94 (d, *J* = 6.6 Hz, 6H), 0.89 (d, *J* = 6.5 Hz, 6H).



1

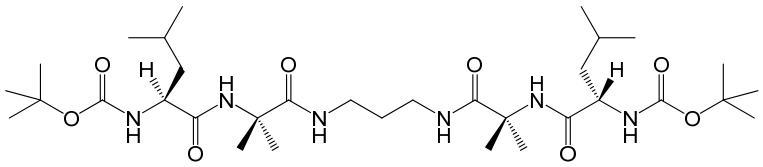
Peptide 1. To 2,2'-bipyridine-5-carbonyl chloride (59.5 mg, 0.272 mmol) were added a solution of N-deprotected peptide **C** (83.4 mg, 0.123 mmol) in dry CH_2Cl_2 (7 mL) and NMM (45.0 μL, 0.41 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 5.5 h. The solvent was evaporated to dryness under reduced pressure. The residue was rinsed with 5 % aqueous $NaHCO_3$ and water. Purification of the residue by column chromatography on silica gel [$CHCl_3$/MeOH (8/2, v/v) as eluent] and further by recrystallization from $CHCl_3$/MeOH/EtOAc/*n*-hexane (ca. 1/1/3/10, v/v/v/v) afforded peptide **1** (65 mg, 50.9 %) as a white solid. HRMS (ESI^+-MS): $[M+Na]^+$ (calcd. 1061.5337) found = 1061.5358. ^1H NMR (500 MHz, DMSO-d_6): δ = 9.18 (dd, *J* = 0.78, 1.4 Hz, 2H), 8.96 (s, 2H), 8.90 (s, 2H), 8.74-8.72 (m, 2H), 8.51-8.43 (m, 6H), 8.19 (t, *J* = 1.9 Hz, 1H), 8.10 (d, *J* = 6.9 Hz, 2H), 7.99 (dt, *J* = 1.8, 5.9 Hz, 2H), 7.76 (s, 2H), 7.51 (dq, *J* = 1.2, 7.5 Hz, 2H), 7.21-7.19 (m, 2H), 7.14-7.11 (m, 1H), 4.07-4.02 (m, 2H), 1.66-1.53 (m+m, 6H), 1.52+1.50+1.47+1.45 (s × 4, 24H), 0.88 (d, *J* = 6.1 Hz, 6H), 0.83 (d, *J* = 6.2 Hz, 6H).



D

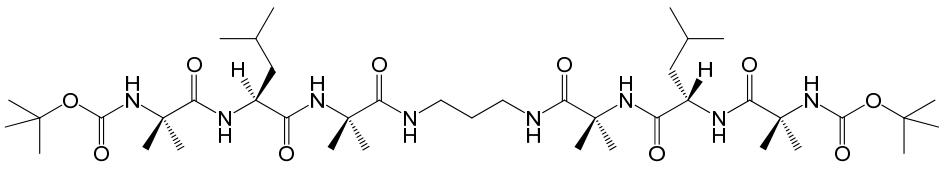
Peptide D. To a solution of Boc-Aib-OH (1.5 g, 7.38 mmol) and HOBt (1.36 g, 8.86 mmol) in DMF (10 mL) was added EDC (1.42 g, 7.38 mmol) at 0 °C. After 30 min, to this was added 1,3-diaminopropane (0.261 g, 3.51 mmol). The reaction mixture was stirred at 0 °C for 2 h and further at room temperature for 18 h. Then, the product was precipitated by adding water (ca. 50 mL) into the solution. Purification of the residue by reprecipitation from $CHCl_3$/MeOH to *n*-hexane provided peptide **D** (1.10 g, 70.3 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 467.28):

found. 467.18. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.59 (t, J = 6.0 Hz, 2H), 6.91 (s, 2H), 3.04 (q, J = 6.1 Hz, 4H), 1.40-1.37 (m+s, 20H), 1.28 (s, 12H).



E

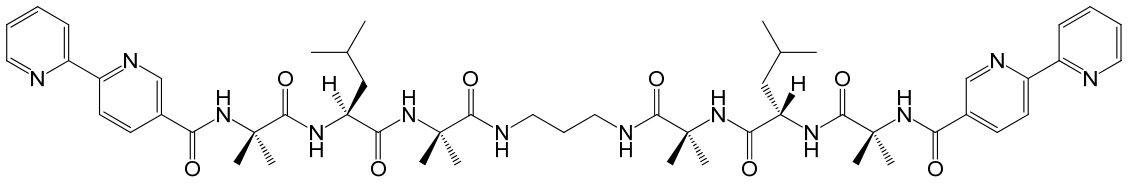
Peptide E. To a solution of Boc-L-Leu-OH (466 mg, 2.01 mmol), HOBt (401 mg, 2.62 mmol), and N-deprotected peptide **D** dihydrochloride (290 mg, 0.912 mmol) in DMF (4 mL) was added EDC (386 mg, 2.01 mmol) at 0 °C. After 30 min, to this was added NMM (207 μL, 1.88 mmol). The reaction mixture was stirred at 0 °C for 3 h and further at room temperature for 9 h. Then, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Purification by column chromatography on silica gel (EtOAc as eluent) afforded peptide **E** (300 mg, 48.8 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 693.45): found. 693.41. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (s, 2H), 6.55 (s, 2H), 5.41 (d, J = 6.2 Hz, 2H), 4.02 (bs, 2H), 3.25 (bs, 4H), 1.71-1.43 (m+m+s+s+s, 38H), 0.95-0.93 (m, 12H).



F

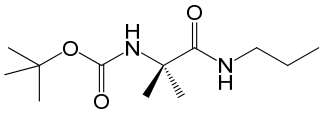
Peptide F. To a solution of Boc-Aib-OH (221 mg, 1.09 mmol), HOBt (200 mg, 1.31 mmol), and N-deprotected peptide **E** dihydrochloride (237 mg, 0.435 mmol) in DMF (2 mL) was added EDC (209 mg, 1.09 mmol) at 0 °C. After 30 min, to this was added NMM (101 μL, 0.914 mmol). The reaction mixture was stirred at 0 °C for 2 h and further at room temperature for 2 days. Then, the

solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Purification of the residue by column chromatography on silica gel [EtOAc/MeOH (95/5, v/v) as eluent] and further recrystallization from $CHCl_3$/*n*-hexane (ca. 1/5, v/v) afforded peptide **F** (204 mg, 57.8 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 863.56): found. 863.51. ^1H NMR (500 MHz, DMSO-d_6): δ = 7.82 (d, *J* = 5.7 Hz, 2H), 7.68 (s, 2H), 7.36 (t, *J* = 5.9 Hz, 2H), 7.16 (s, 2H), 4.04 (bs, 2H), 3.01 (q, *J* = 6.2 Hz, 4H), 1.63-1.39 (m+m+s, 26H), 1.36+1.35+1.30+1.29 (s × 4, 24H), 0.86 (d, *J* = 6.3 Hz, 6H), 0.82 (d, *J* = 6.2 Hz, 6H).



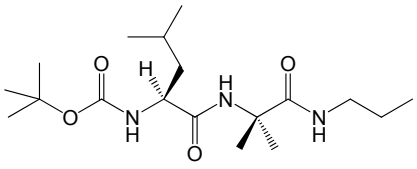
2

Peptide 2. To a suspension of 2,2'-bipyridine-5-carbonyl chloride (123 mg, 0.562 mmol) in dry CH_2Cl_2 (2 mL) was added a solution of N-deprotected peptide **F** dihydrochloride (167 mg, 0.234 mmol) in dry CH_2Cl_2 (6 mL) containing DIEA (210 μL, 1.26 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 h and the solution was then evaporated to dryness under reduced pressure. Purification of the residue by washing with 5 % aqueous $NaHCO_3$ and water and further by column chromatography on silica gel [$CHCl_3$/MeOH (9/1, v/v) as eluent] afforded peptide **2** (165 mg, 70.5 %) as a white solid. HRMS (ESI^+-MS): $[M+Na]^+$ (calcd. 1027.5494) found = 1027.5498. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.11 (dd, *J* = 0.69, 1.6 Hz, 2H), 8.70-8.69 (m, 2H), 8.47 (dd, *J* = 0.68, 8.3 Hz, 2H), 8.44-8.42 (m, 2H), 8.24 (dd, *J* = 2.3, 8.3 Hz, 2H), 7.84 (dt, *J* = 1.8, 7.7 Hz, 2H), 7.41 (s, 2H), 7.37-7.35 (m, 2H), 7.25-7.22 (m, 4H), 7.20 (s, 2H), 4.53 (m, 2H), 2.85 (m, 2H), 2.58 (m, 2H), 1.88 (m, 2H), 1.66-1.54 (s+s+s+s+m+m, 30H), 0.97-0.95(m, 12H).



G

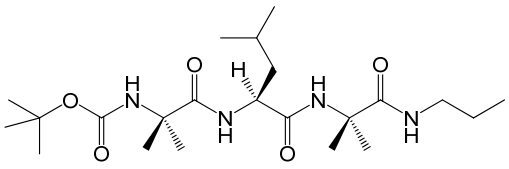
Peptide G (Boc-Aib-NH-C_3H_7). To a solution of Boc-Aib-OH (500 mg, 2.46 mmol) and HOBt (452 mg, 2.95 mmol) in DMF (3 mL) was added EDC (472 mg, 2.46 mmol) at 0 °C. After 30 min, to this was added propylamine (145 mg, 2.46 mmol). The reaction mixture was stirred at 0 °C for 2 h and further at room temperature for 16 h. Then, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Recrystallization from EtOAc/*n*-hexane (ca. 1/5, v/v) provided peptide **G** (365 mg, 60.7 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 267.17): found. 267.09. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.51 (bs, 1H), 4.89 (bs, 1H), 3.22 (dt, *J* = 7.0, 5.8 Hz, 2H), 1.52 (sex, *J* = 7.2 Hz, 2H), 1.48 (s, 6H), 1.44 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H).



H

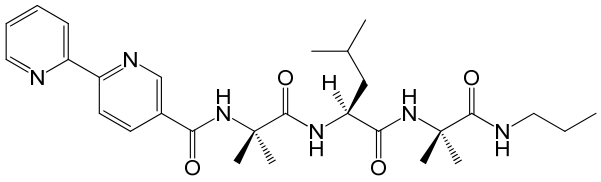
Peptide H (Boc-L-Leu-Aib-NH-C_3H_7). To a solution of Boc-L-Leu-OH (355 mg, 1.53 mmol), HOBt (291 mg, 1.90 mmol), and N-deprotected peptide **G** hydrochloride (235 mg, 1.46 mmol) in DMF (2 mL) was added EDC (294 mg, 1.534 mmol) at 0 °C. After 30 min, to this was added NMM (161 μL, 1.46 mmol). The reaction mixture was stirred at 0 °C for 3 h and further at room temperature for 2 days. Then, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Recrystallization from $CHCl_3$/*n*-hexane (ca. 1/6, v/v) afforded peptide **H** (378 mg, 72.4 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 380.25):

found. 380.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.80 (bs, 1H), 6.37 (bs, 1H), 4.85 (bs, 1H), 3.93-3.89 (m, 1H), 3.26-3.12 (m, 2H), 1.56-1.45 (m+m+s+s, 18H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).



I

Peptide I (Boc-Aib-L-Leu-Aib-NH-C_3H_7). To a solution of Boc-Aib-OH (224 mg, 1.10 mmol), HOBt (202 mg, 1.32 mmol), and N-deprotected peptide **H** hydrochloride (304 mg, 1.04 mmol) in DMF (2 mL) was added EDC (211 mg, 1.10 mmol) at 0 °C. After 45 min, to this was added NMM (120 μL, 1.09 mmol). The reaction mixture was stirred at 0 °C for 3 h and further at room temperature for 3 days. Then, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 1N aqueous HCl, 5 % aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. Recrystallization from EtOAc/*n*-hexane (ca. 1/5, v/v) afforded peptide **I** (398 mg, 86.9 %) as a white solid. MALDI-TOF-MS: $[M+Na]^+$ (calcd. 465.30): found. 465.15. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 (bs, 1H), 6.89 (m, 1H), 6.51 (d, *J* = 5.7 Hz, 1H), 4.90 (s, 1H), 4.08-4.04 (m, 1H), 3.22-3.18 (m, 2H), 1.80-1.75 (m, 1H), 1.71-1.63 (m, 1H), 1.58 (s, 3H), 1.57-1.52 (m+m, 3H), 1.51+1.48+1.46+1.43 (s × 4, 21H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.93-0.90 (m, 6H).



3

Peptide 3. To a suspension of 2,2'-bipyridine-5-carbonyl chloride (89 mg, 0.407 mmol) in dry CH_2Cl_2 (2 mL) was added a solution of N-deprotected peptide **I** hydrochloride (128 mg, 0.339 mmol) in dry CH_2Cl_2 (3 mL) containing DIEA (195 μL, 1.175 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 3 h, the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, and the solution was washed with 5 % aqueous $NaHCO_3$ and dried over $MgSO_4$. Purification of the residue by column chromatography on silica gel [EtOAc to EtOAc/MeOH (95/5, v/v) as eluent] afforded peptide **3** (174 mg, 98.0 %) as a white solid. HRMS (ESI^+-MS): $[M+Na]^+$ (calcd. 547.3009) found = 547.3018. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.08 (dd, *J* = 0.80, 2.3 Hz, 1H), 8.73-8.71 (m, 1H), 8.52 (dd, *J* = 0.77, 8.3 Hz, 1H), 8.47-8.45 (m, 1H), 8.19 (dd, *J* = 2.3, 8.3 Hz, 1H), 7.86 (dt, *J* = 1.8, 7.7 Hz, 1H), 7.39-7.37 (m, 1H), 7.14 (s, 1H), 6.87 (s, 1H), 6.79 (t, *J* = 5.6 Hz, 1H), 6.48 (d, *J* = 6.3 Hz, 1H), 4.21-4.17 (m, 1H), 3.17 (dt, *J* = 7.1, 5.7 Hz, 2H), 1.82-1.77 (m, 1H), 1.69 (s, 3H), 1.68 (s, 3H), 1.63-1.56 (m+s+s, 8H), 1.55-1.47 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H).

General Procedure for the Preparation of Fe^{II} Complexes. Complex C1, $[Fe_2(1)_3](BF_4)_4$: A solution of $Fe(BF_4)_2{\cdot}6H_2O$ (4.75 mg, 14.1 μmol) in dexoygenated MeOH (5.0 mL) was prepared under argon, and a 1.0 mL aliquot of the solution was transferred to a flask with a stopcock and then diluted 50 times with deoxygenated MeOH. A stock solution of peptide **1** (1.08 mg, 1.04 μmol) in dexoygenated MeOH (25 mL) was also prepared under argon. To a 2.0 mL (83.1 nmol) aliquot of the stock solution of peptide **1** was added a 1.0 mL (56.3 nmol) aliquot of the diluted $Fe(BF_4)_2{\cdot}6H_2O$ solution under argon. The solution color immediately changed to red-violet and used to CD, absorption, and CSI-MS measurments.

Supporting References

(S1) Y. Cohen,; L. Avram,; L. Frish, *Angew. Chem., Int. Ed*., 2005, **44**, 520.

(S2) U. Kiehne, J. Bunzen, H. Staats and A. Lützen, *Synthesis* 2007, 1061.

Additional Spectroscopic Data

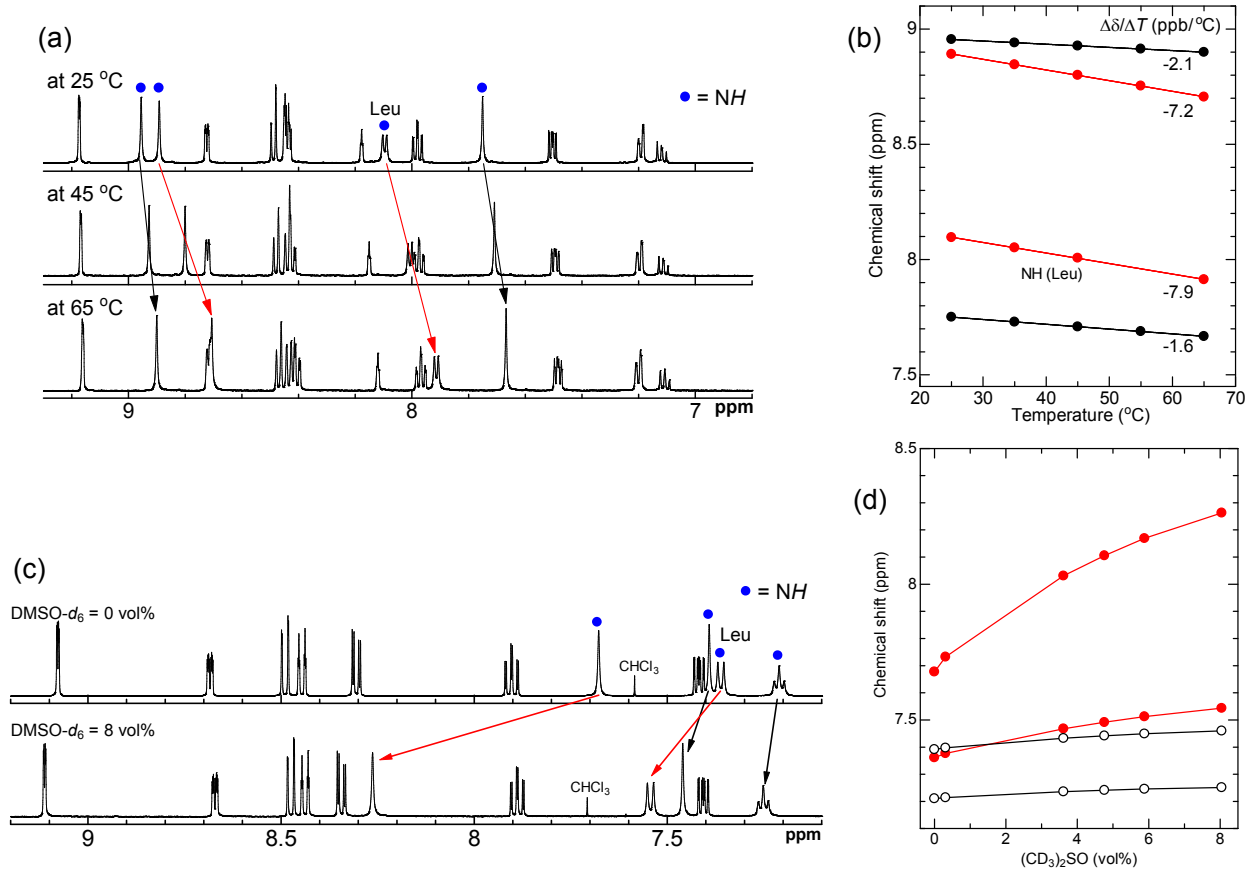


Fig. S1 (a) Variable-temperature ^{1}H NMR spectra of **1** in DMSO-d_6; [**1**] = 3.0 mM. (b) Plots of the NH chemical shifts in the ^{1}H NMR spectra of **1** as a function of temperature in DMSO-d_6. (c) ^{1}H NMR spectra of **2** in CD_3CN (upper) and CD_3CN/DMSO-d_6 mixture (92/8; v/v) (bottom) at room temperature. (d) Solvent dependence on the NH chemical shifts of **2** in CD_3CN/DMSO-d_6 mixtures.

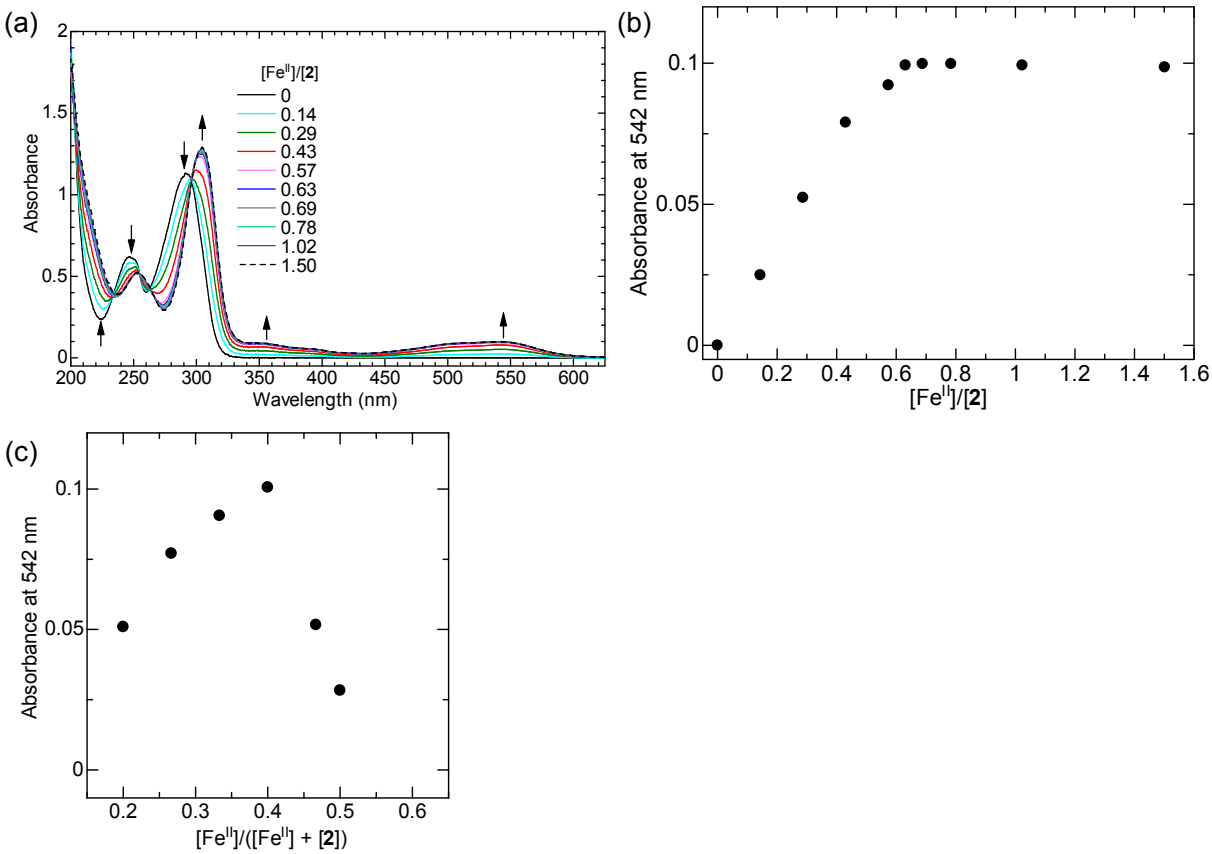


Fig. S2 (a) UV-vis absorption spectral changes of **2** in CH_3CN at room temperature upon the addition of $Fe(BF_4)_2$; $[\mathbf{2}]_0 = 8.8 \times 10^{-6}$ M. (b) Plots of the absorbance of **2** at 542 nm against variable $[Fe^{II}]/[\mathbf{2}]$ ratios. (c) Job's plot of ligand **2** with $Fe(BF_4)_2$ in CH_3CN at room temperature. The total concentration ($[\mathbf{2}] + [Fe^{II}]$) is 4.3×10^{-5} M.

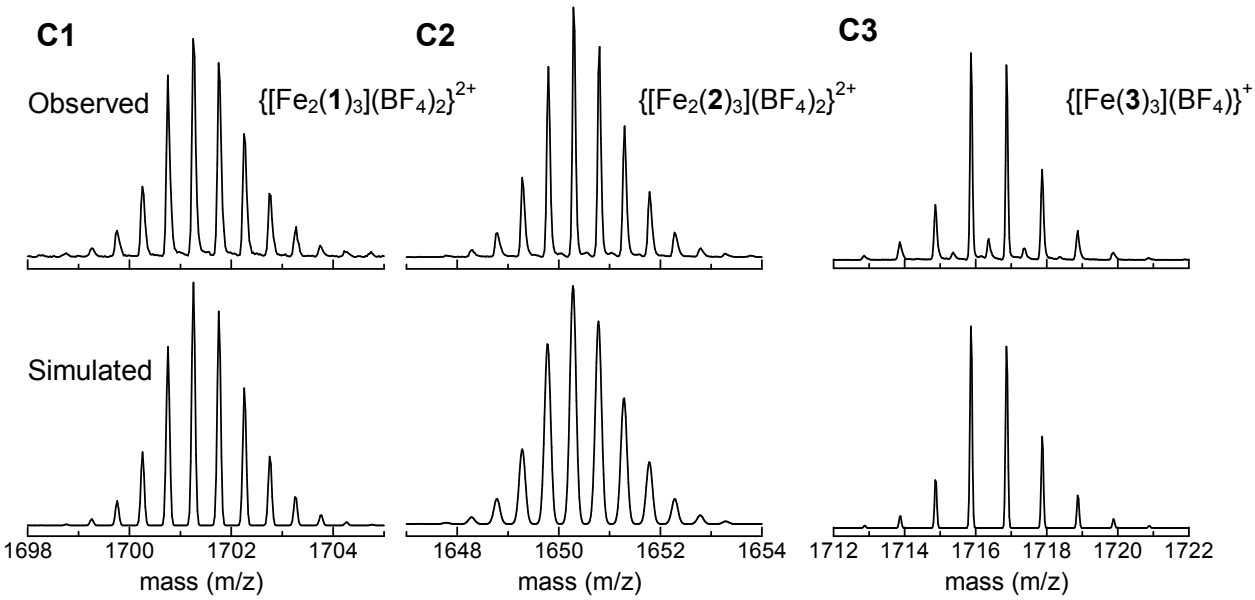


Fig. S3 Experimental (upper) and simulated (bottom) cold-spray ionization mass spectra of the Fe^{II} complexes **C1**, **C2**, and **C3**.

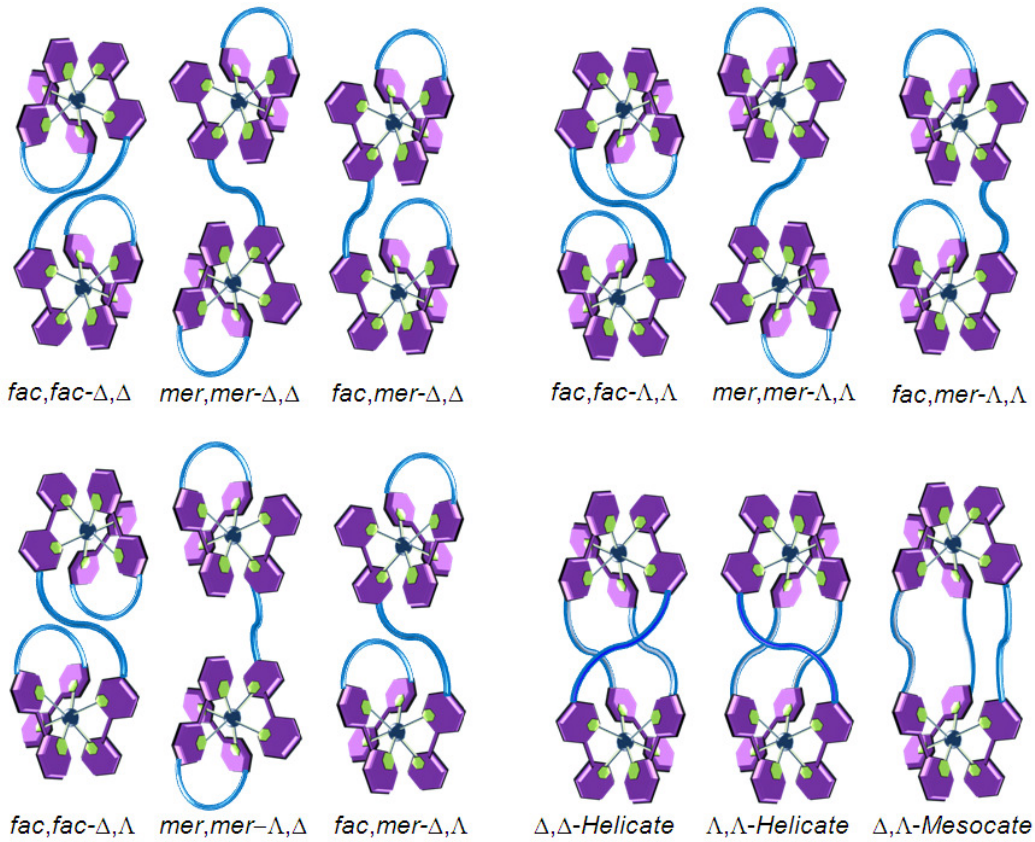


Fig. S4 Schematic representation of possible regio- and stereoisomers of the complexes **C1** and **C2**.

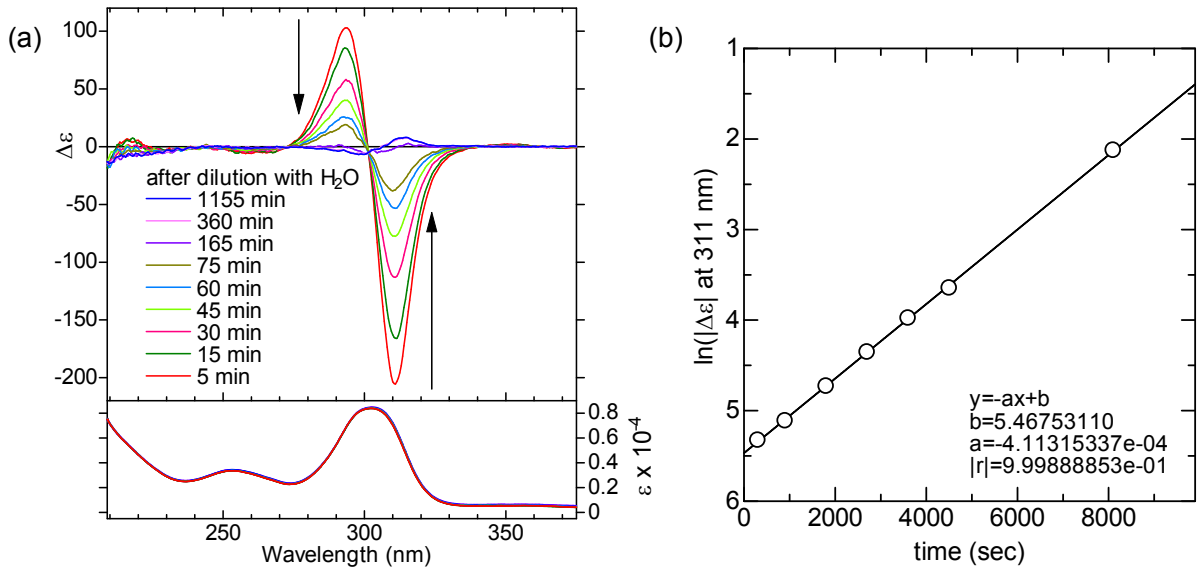


Fig. S5 (a) Time-dependent CD (upper) and absorption (bottom) spectral changes of a CD_3CN solution of **C2** after dilution with H_2O at 25 ºC; H_2O/CD_3CN (20/1; v/v), [**C2**] = 8.8×10^{-6} M. Δε and ε values were calculated based on the molar concentration of $Fe(bpy)_3$ moiety in **C2**. (b) Plot of ln(|Δε| at 311 nm) with time.