Supporting Information for

Chirality-Organized Ferrocene Receptor Bearing Podand Dipeptide Chains (-L-Ala-L-Pro-NHPyMe) for the Selective Recognition of Dicarboxylic Acids

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General Comments

All reagents and solvents were purchased from commercial sources and were further purified by the 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 Varian MERCURY 300 (300 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer.

Preparation of the ferrocene 1 bearing podand dipeptide chains (-L-Ala-L-Pro-NHPyMe).

To a stirred mixture of H-L-Ala-L-Pro-NHPyMe (138.2 mg, 0.50 mmol) and triethylamine (348 μL, 2.5 mmol) in CH_2Cl_2 (5 mL) was dropwise added 1,1'-bis(chlorocarbonyl)ferrocene (77.7 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) under argon at 0 °C. The

mixture was stirred at 0 °C for 1 h and then at room temperature for 4 h. The resulting mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo. Purification was performed by a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC, $CHCl_3$ as an eluent). The ferrocene **1** was isolated in 70% yield by recrystallization from $CHCl_3$. Mp 148-150 °C (uncorrected); IR (CH_2Cl_2, 1.0 x 10^{-3} M): 3399, 3307, 1697, 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 5.0 x 10^{-3} M): δ 8.84 (d, 2H, J = 7.2 Hz), 8.78 (s, 2H), 7.91 (d, 2H, J = 8.4 Hz), 7.55 (dd, 2H, J = 8.4, 7.5 Hz), 6.87 (d, 2H, J = 7.5 Hz), 4.90-4.88 (m, 4H), 4.86-4.74 (m, 4H), 4.54-4.52 (m, 2H), 4.31-4.29 (m, 2H), 3.99-3.91 (m, 2H), 3.71-3.66 (m, 2H), 2.45-2.11 (m, 14H), 1.33 (d, 6H, J = 7.2 Hz); FAB-MS m/z 791 (M^++1); Anal. Calcd for $C_{40}H_{46}N_8O_6Fe \cdot H_2O$: C, 59.41; H, 5.98; N, 13.86. Found: C, 59.07; H, 5.64; N, 13.47.

Preparation of the ferrocene 2 bearing one dipeptide chain (-L-Ala-L-Pro-NHPyMe).

To a stirred solution of H-L-Ala-L-Pro-NHPyMe (65.6 mg, 0.25 mmol) and triethylamine (139 μL, 1.0 mmol) in CH_2Cl_2 (5 mL) was dropwise added (chlorocarbonyl)ferrocene (62.1 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) under argon at 0 °C. The mixture was stirred at 0 °C for 1 h and then at room temperature for 4 h. The resulting mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo. Purification was performed by a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC, using $CHCl_3$ as an eluent). The ferrocene **2** was isolated in 54% yield by recrystallization from $CHCl_3$. Mp 95-97 °C (uncorrected); IR (CH_2Cl_2, 2.0 x 10^{-3} M): 3411, 1701, 1636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1.0 x 10^{-2} M): δ 8.86 (s, 1H), 7.96 (d, 1H, J = 8.1 Hz), 7.57 (dd, 1H, J = 8.1,

7.2 Hz), 6.89 (d, 1H, J = 7.2 Hz), 6.69 (d, 1H, J = 7.5 Hz), 4.99-4.90 (m, 1H), 4.74-4.69 (m, 3H), 4.35-4.34 (m, 2H), 4.22 (s, 5H), 3.87-3.79 (m, 1H), 3.74-3.67 (m, 1H), 2.45 (s, 3H), 2.38-2.32 (m, 1H), 2.24-2.06 (m, 3H), 1.50 (d, 3H, J = 6.6 Hz); FAB-MS m/z 489 (M^++1); Anal. Calcd for $C_{25}H_{28}N_4O_3Fe{\cdot}H_2O$: C, 59.30; H, 5.97; N, 11.06. Found: C, 58.93; H, 6.08; N, 10.67.

CD Measurements.

CD spectra were recorded using a JASCO J-720 spectropolarimeter in the deaerated CH_3CN solution with the concentration (1.0×10^{-4} M) under argon at 25 °C.

Determination of Stoichiometry and Association Constants.

In seven separate 5-mm-o.d. NMR tubes **1** and **3c** were mixed changing ratio from 0 to 1 while maintaining a total concentration 5.0×10^{-3} M ($CDCl_3$/acetone-d_6 (5/1)) under argon at 25 °C. The chemical shift of N*H* adjacent to the pyridyl moiety of **1** was recorded for each sample. The stoichiometry of receptor-guest complex formation was determined by using Job plots. Job plots for the complexation of **1** and **3c** was shown in Figure S2. The association constants were calculated by fitting the data to a 1:1 binding isotherm using the program , kindly provided by Dr. K. Hirose at Osaka University (Naemura, K.; Fuji, J.; Ogasahara, K.; Hirose, K.; Tobe, Y. *Chem. Commun.* **1996**, 2749; Naemura, K.; Nishikawa, Y.; Fuji, J.; Hirose, K.; Tobe, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 873.).

X-ray Structure Analysis.

All measurements for **1** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structure of **1** was 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 S1.