Synthesis of Ferrocenyl and Diphenyl Substituted Bispyridino-18-Crown-6 Ether for Chiral Recognition†

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The article reports the synthesis of a novel bispyridino-18-crown-6 ether, 7-{[(5S,15S)-5,15-diphenyl-3,6,14,17-tetraoxa-23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptyl-ferrocenamide **6**, bearing the C_2-symmetric diphenyl substituents as chiral barriers and the ferrocenyl groups serving as an electrochemical sensor, and its electrochemical study with *D*- and *L*-AlaOMe·HCl as the guest by cyclovoltametry.

Key Words : Chiral crown ether, Bispyridine-18-crown-6, Chiral recognition, Ferrocenyl group, Chemical sensor

Introduction

Molecular recognition is ubiquitous in nature.[1] Examples include the antibody-antigen interaction, the biochemical catalysis reactions,[2] the DNA double helix and the incorporation of the single diastereomeric form of amino acids and sugar in metabolic pathway.[3] On the other hand, molecular recognition has also been applied in various areas of the analytical chemistry, such as chromatography as well as NMR and Mass spectroscopies.[4]

The chiral crown ethers have shown successful chiral discrimination, illustrated by various types of the host molecules.[5] Many macrocyclic ligand possessing a redox active moiety were reported.[6] For a few recent years, one of our research topic has been the synthetic development of new chiral macrocycle hosts and their applications for molecular recognitions.[7] We herein report the synthesis of the macrocyclic ligand **6** bearing a C_2-symmetric diphenyl substituted bispyridino 18-crown-6 backbone, which would presumably be a good potential host, and a ferrocenyl group serving as a versatile chemical sensor.[8] The enantiomeric recognition of the redox active chiral macrocycle was investigated using cyclovoltametry technique. Cyclovoltamograms were recorded with the different concentrations of *D* and *L*-AlaOMe·HCl in the presence of the macrocycle.

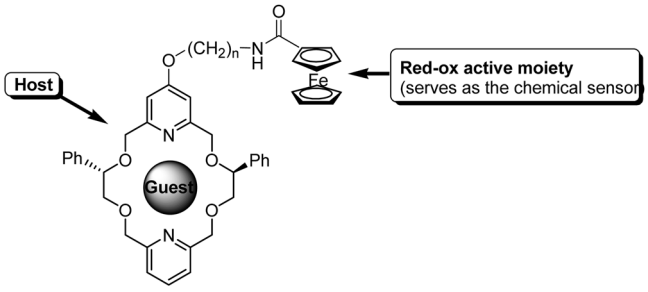


Chart 1. Guest bound in the macrocyclic chiral host with redox active moiety.

†This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

Experimental Section

General. ^{1}H-NMR, and ^{13}C-NMR spectra were recorded on a Varian Gemimi 200 (200 MHz). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under fast atom bombardment (FAB) conditions with nitrobenzyl alcohol (NBA) as the matrix in the Korea Basic Science Institute (Daegu), Korea. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.040-0.063 mm). Analytical thin layer chromatography (TLC) was performed using pre-coated TLC plates with silica Gel 60 F_{254} (E. Merck no. 5715-7). All reactions were carried out under argon atmosphere with dry solvent, unless otherwise noted. Tetrahydrofuran (THF), and diethyl ether were distilled from sodium/benzophenone immediately prior to use and methylene chloride (CH_2Cl_2) was dried from calcium hydride. All chemicals were reagent grade unless otherwise specified. The (*D*)-, and (*L*)-alanine methyl esters were obtained from Aldrich Chemical Co.. (1S)-2-({[6-({[(2S)-2-hydroxy-2-phenylethyl]oxy}methyl)-2-pyridinyl]methyl}oxy)-1-phenylethanol (**2**), was prepared using our previously reported methods.[7]

Diethyl 4-pyridine-2,6-dicarboxylate (1). Chelidamic acid, 4-oxo-1,4-dihydro-2,6-pyridinedicarboxylic acid (3 g, 0.015 mol), was added into the solution of sulfuric acid in 140 mL of ethanol. The reaction mixture was refluxed for 24 h, then cooled, and concentrated *in vacuo*. The residue was treated with water, neutralized with $NaHCO_3$, and acidified with *conc.* HCl. Obtained solid was dried and purified by flash chromatography to afford diethyl 4-pyridine-2,6-dicarboxylate (**1**) (3.91 g, 99%) as an yellow oil: (R_f = 0.27, SiO_2, 5% MeOH/CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.76 (s, 2H), 4.48 (q, 4H), 1.42 (t, 6H).

Diethyl 4-[(6-cyanohexyl)oxy]-2,6-pyridinedicarboxylate (2). A mixture of dicarboxylate compound **1** (8.00 g,

33.44 mmol) and K_2CO_3(93 g, 50.16 mmol) in acetone was stirred at room temperature for 30 min., and then 1,7-bromoheptanitrile (10.0 mL, 66.88 mmol) was added. The reaction mixture was refluxed for 7 h, diluted with ethyl acetate and washed with water. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography to give 11.50 g (98.7%) of diethyl 4-[(6-cyanohexyl)oxy]-2,6-pyridinedicarboxylate (**2**); (R_f = 0.29, SiO_2, ethyl acetate:hexane = 1:1) as an orange oil: ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.43 (6H, t, J = 7.0 Hz), 1.50-1.99 (8H, m), 2.36 (2H, t, J = 6.6 Hz) 4.12 (2H, t, J = 6.6 Hz), 4.41-4.50 (4H, q, J = 7.0 Hz), 7.74 (2H, s).

7-{[2,6-Bis(hydroxymethyl)-4-pyridinyl]oxy}heptanenitrile (3). To a stirred solution of the cyano compound **2** (11.50 g, 33.01 mmol) in ethanol was added 3.74 g (99.02 mmol) of $NaBH_4$ and 4.39 g (39.60 mmol) of $CaCl_2$ at 0 °C. The resulting mixture was stirred at room temperature for 4 h under argon atmosphere, then diluted with ethyl acetate and washed with water. The organic phase was dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography to provide 7-{[2,6-bis(hydroxymethyl)-4-pyridinyl]oxy}heptanenitrile (**3**) as an orange oil in 98.8% (8.60 g) yield: (R_f = 0.07, SiO_2, ethyl acetate). ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.52-1.82 (m, 8H), 2.37 (t, 2H, J = 6.6 Hz), 4.03 (t, 2H, J = 6.6 Hz), 4.70 (s, 4H), 6.69 (s, 2H).

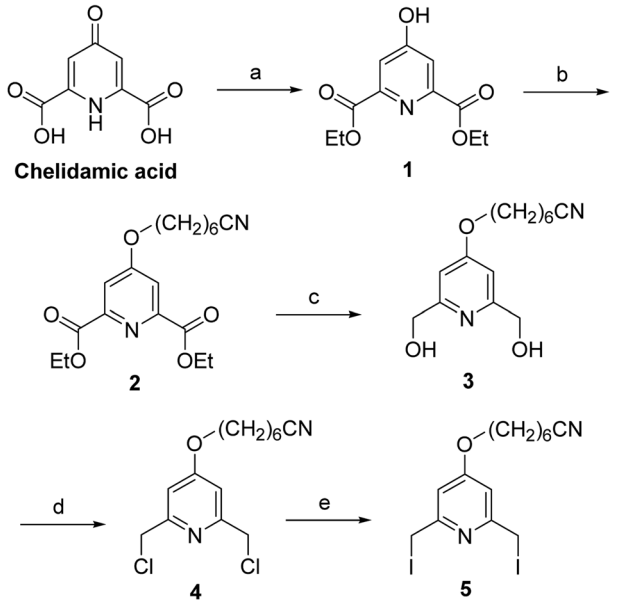
7-{[2,6-Bis(chloromethyl)-4-pyridinyl]oxy}heptanenitrile (4). The diol compound **3** (8.60 g, 32.54 mmol) were added to 30 mL of thionyl chloride at room temperature. The solution was stirred at 70 °C for 5 h, cooled to room temperature, and concentrated under reduced pressure. Crushed ices were added to the residues and the resulting suspensions were neutralized with 10% aq. Na_2CO_3, diluted with ethyl acetate, and washed with water. The organic phase was dried with magnesium sulfate, concentrated under reduced pressure, and purified by flash chromatography to afford 7-{[2,6-bis(chloromethyl)-4-pyridinyl]oxy}heptanenitrile (**4**) (9.41 g, 96.1%) as an orange oil; (R_f = 0.26, SiO_2, ethyl acetate:hexane = 1:2): ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.48-1.84 (m, 8H), 2.38 (t, 2H, J = 6.6 Hz), 4.01 (t, 2H, J = 8.0 Hz), 4.60 (s, 4H), 6.94 (s, 2H).

7-{[2,6-Bis(iodomethyl)-4-pyridinyl]oxy}heptanenitrile (5). To a solution of the dichloride compound **4** (4.26 g, 14.19 mmol) in acetone was added 6.38 g (42.57 mmol) of sodium iodide at room temperature. The reaction mixture was refluxed for 24 h, cooled, and concentrated under reduced pressure. The residue was diluted with ether and washed with water. The organic phase was dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography to give 5.72 g (83.6%) of 7-{[2,6-bis(iodomethyl)-4-pyridinyl]-oxy}heptanenitrile (**5**) as an orange oil: (R_f = 0.26, SiO_2, ethyl acetate:hexane = 1:2). ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.48-1.66 (m, 4H), 1.72-1.84 (qui, 4H, J = 3.0 Hz), 2.38 (t, 2H, J = 6.6 Hz), 4.02 (t, 2H, J = 8.0 Hz), 4.42 (s, 4H), 6.76 (s, 2H).

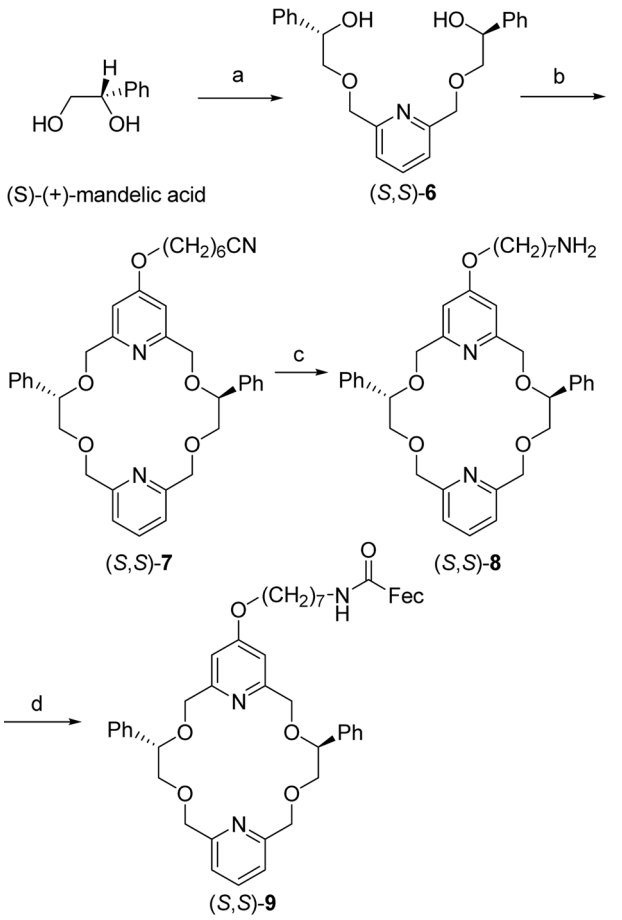
7-{[(5S,15S)-5,15-Diphenyl-3,6,14,17-tetraoxa-23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptanenitrile (7). To a stirred suspension of NaH (0.38 g, 7.91 mmol, 60% dispersion in mineral) in 10 mL of THF was added 1.00 g (2.64 mmol) of (*S,S*) diol **6** dissolved in 30 mL of THF at room temperature. The reaction mixture was stirred at room temperature for 10 min, refluxed for 2.5 h, cooled to 0 °C, and treated with diiodide **5** (1.27 g, 2.64 mmol) in THF. The reaction mixture was stirred at 0 °C for 3 h, and then at room temperature for 3 days. The resulting mixture was concentrated under reduced pressure, diluted with CH_2Cl_2 and washed with distilled water. The organic phase was concentrated under reduced pressure, and purified by flash chromatography to give the desired 7-{[(5S,15S)-5,15-diphenyl-3,6,14,17-tetraoxa-23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptanenitrile (**7**) as an orange oil in 22.3% (0.34 g) yield: (R_f = 0.23, SiO_2, 5% MeOH/CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.51-1.67 (m, 4H), 1.70-1.89 (m, 4H), 2.37 (t, 2H, J = 8.6 Hz), 3.62-3.77 (dd, 2H, J = 12.2 Hz, 2.8 Hz), 3.80-3.97 (m, 2H), 4.30-4.84 (m, 10H), 6.67 (s, 2H), 7.23-7.38 (m, 12H), 7.69(t, 1H, J = 8.2 Hz).

7-{[(5S,15S)-5,15-Diphenyl-3,6,14,17-tetraoxa-23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptanamine (8). A solution of 0.34 g (0.56 mmol) of the macrocycle nitrile **7** in dry 2 mL of ether were added dropwise to the stirred suspension of $LiAlH_4$ (0.03 g, 0.84 mmol) in 5 mL ether at 0 °C. The reaction mixture was stirred for 19 h at room temperature. After dilution with ether, the organic phase was concentrated under reduced pressure, and purified by flash chromatography to give 0.10 g (29.8%) of 7-{[(5S,15S)-5,15-diphenyl-3,6,14,17-tetraoxa-23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptanamine (**8**) as an orange oil: (R_f = 0.07, SiO_2, 15% MeOH/CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.41-1.57 (m, 6H), 1.71-1.90 (m, 4H), 2.75 (t, 2H, J = 7.2 Hz), 3.66-3.80 (dd, 2H, J = 12.0 Hz, 2.8 Hz), 3.81-4.04 (m, 2H), 4.41-4.90 (m, 10H), 6.36 (s, 2H), 7.26-7.41 (m, 12H), 7.65 (t, 1H, J = 7.4 Hz).

7-{[(5S,15S)-5,15-Diphenyl-3,6,14,17-tetraoxa-23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptylferrocenamide (9). To a stirred suspension of oxalyl chloride (3 mL, excess) in methylene chloride and pyridine as catalyst was added ferrocenecarboxylic acid (0.230 g, 1.0 mmol) in methylene chloride. The reaction mixture was stirred for 4 h at room temperature, and then concentrated under reduced pressure. The residue was dissolved again in ether, filtered, and evaporated *in vacuo* to obtained chlorocarbonylferrocene (0.248 g, 100%) as a dark orange solid. To a solution of macrocycle amine **8** (0.10 g, 0.16 mmol) in methylene chloride containing triethylamine was added a solution of chlorocarbonylferrocene in methylene chloride slowly over 30 min at room temperature. The mixture was stirred at room temperature for 4 h, the solvent was evaporated, and the crude mixture was purified by flash chromatography to afford the final macrocycle, 7-{[(5S,15S)-5,15-diphenyl-3,6,14,17-tetraoxa-



Scheme 1. *Reaction conditions*; (a) H_2SO_4, EtOH, reflux, 24 h, 99%; (b) 1,7-bromoheptanitrile, K_2CO_3, acetone, reflux, 7 h, 98.7%; (c) $NaBH_4$, $CaCl_2$, EtOH, RT, 4 h, 98.8%; (d) $SOCl_2$, reflux, 5 h, 96.1%; (e) NaI, acetone, reflux, 24 h, 83.6%.



Scheme 2. *Reaction conditions*; (a) 71% over 4 steps from (*S*)-(+)-mandelic acid *via* previously reported procedure[7]; (b) NaH, Compound **5**, THF, RT, 3 days, 22.3%; (c) $LiAlH_4$, Et_2O, CH_2Cl_2 RT, 15 h, 29.8%; (d) Chlorocarbonylferrocene, TEA, CH_2Cl_2, RT, 4 h, 23.1%.

23,24-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8(24),9,11,19,21-hexaen-10-yl]oxy}heptylferrocenamide (**9**), (0.03 g, 23.1%) as an orange oil: (R_f = 0.25, SiO_2, 5% MeOH/CH_2Cl_2). ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.31-1.50 (m, 6H), 1.62-1.89 (m, 4H), 3.32 (t, 2H, J = 6.6 Hz), 3.62-3.76 (dd, 4H, J = 11.2 Hz, 2.7Hz) 3.72-3.91 (m, 4H), 4.21 (s, 5H), 4.30 (s, 2H), 4.55 (s, 2H), 4.60-5.05 (m, 10H), 6.63 (s, 2H), 7.27-7.40 (m, 12H), 7.68 (t, 1H, J = 8.0 Hz); HRMS (FAB, NBA) calcd 824.3357 for $C_{47}H_{51}FeN_3O_6$ $(M+H)^+$, found 824.3365.

Results and Discussion

The general synthetic routes toward the macrocyclic compounds are outlined in Scheme 1 and 2. The C_2-symmetric diphenyl substituted macrocyclic host was prepared from the commercially available and optically pure (*S*)-mandelic acid. The pyridino diiodide **5** was synthesized from chelidamic acid over 5 steps in 70% yield. The chiral subunit (*S,S*) diol **6** was prepared from (*S*)-(+)-mandelic acid over 4 steps in 71% yield *via* our previously reported route.[7] The (*S,S*) diol **6** was coupled with the 2,6-bis(iodomethyl)pyridine **5** using sodium hydride in THF to afford (*S,S*) cyano compound **7** in 22% yield. The cyano group of the macrocycle **7** was reduced to generate the amino substituted marcocycle **8** in 30% yield, which was converted to the desired ferrocene substituted macrocycle **9** in 23% yield by using chlorocarbonylferrocene. The novel C_2-symmetic bispyridino-18-crown-6 ether (*S,S*) ferrocene compound **9** bearing two diphenyl substituents as the chiral barriers and the ferrocene group as the electrochemical sensor was synthesized for the enantiomeric recognition of the chiral amino acid esters. The structure of the ferrocenyl and diphenyl substituted new chiral macrocycle ligand was determined by NMR spectroscopy data and FAB-MS analysis.

The new chiral crown ether (*S,S*)-**9** was designed and synthesized in such a way that the interaction options available for the incoming chiral amino acid ester hydrochloride are limited. As shown in Figure 1, the complex is possible to have tripod hydrogen bonding between one nitrogen and two oxygens of the host and three hydrogen atoms of the ammonium cation of the guest. NH^+-N hydrogen bond interaction of the ammonium cation to the pyridine nitrogen is generally favored than the NH^+-O hydrogen bond.[9] In addition to this, another hydrogen bonding interactions between amide hydrogens of the host and carbonyl oxygen of the guest could be possible to exist. With these possible hydrogen bonding interactions between the chiral crown ether (*S,S*)-**9** and AlaOMe·HCl, the complex with the *D*-AlaOMe·HCl will have less severe steric repulsion between the methyl group on the chiral carbon of AlaOMe·HCl and the phenyl group of the host. This steric repulsion will give one of the possible explanations of the higher affinity in case of *D*-AlaOMe·HCl as compared to that of *L*-AlaOMe·HCl.

It is possible to detect the enantiomercic recognition by the

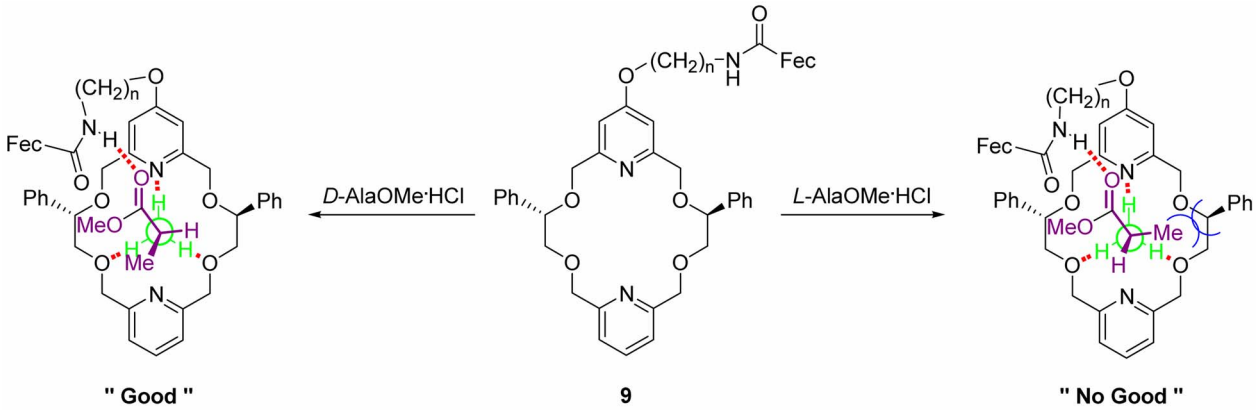


Figure 1. Illustration of the interaction between the macrocycle and *D*,*L*-AlaOMe·HCl.

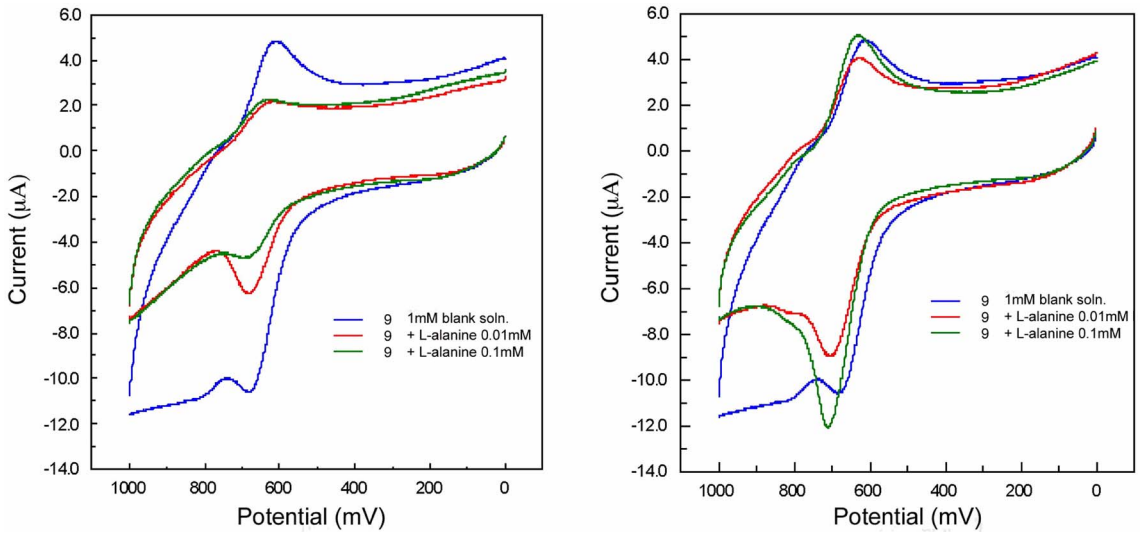


Figure 2. Cyclovoltamograms of the new macrocycle and *D*,*L*-AlaOMe·HCl.

electrochemical methods, such as cyclovoltametry through the introduction of ferrocenyl group.[10,8a] Cyclovoltamograms were recorded with the different concentrations of *D*-AlaOMe·HCl and *L*-AlaOMe·HCl in the presence of the new chiral macrocycle bearing the redox active chemical sensor, as shown in Figure 3. The blank solution of the macrocycle **9** was prepared as 1mM in $CHCl_3$, and its cyclovoltamogram was examined at the ambient temperature. The sample solutions of *D*-AlaOMe·HCl and *L*-AlaOMe·HCl were prepared as 0.01 mM and 0.1 mM in $CHCl_3$. The macrocycle possessing the ferrocenyl group with *D*-AlaOMe·HCl showed the voltage difference (~20 mV), whereas *L*-AlaOMe·HCl provided no change. The observed electrochemical difference of the macrocycle with enatiomeric amino esters supports the preliminary hypothesis showing that *L*-AlaOMe·HCl has lower affinity to the host than *D*-AlaOMe·HCl.

Conclusions

In conclusion, we report the design and synthesis of a new C_2-symmetic bispyridino-18-crown-6 ether (*S*,*S*)-**9** bearing two diphenyl substituents and a ferrocenyl group as an electrochemical sensor. The synthesized chiral bispyridino-18-crown-6 **9** was investigated for the electrochemical chiral recognition *via* cyclovotametry at ambient temperature. The cyclovotamograms showed the different electrochemical effect on the coordination of the macrocycle **9** and *D*-AlaOMe·HCl and *L*-AlaOMe·HCl.

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