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Self-Assembly of Twisted Bridging Ligands to Helical Coordination Polymers

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The design and synthesis of polynuclear complexes possessing ordered conformations has been an attractive field in recent years.[1] Helical conformation of polynuclear complexes (helicates) has been established by the self-assembly processes of ligands with metal ions.[2] Recently, several groups have reported the chiral effects on the determination of the sense of helicates.[3] The control of right- (*P*) and left-handed (*M*) chirality of helicates in self-assembly processes was accomplished by the use of enantiomerically pure chiral ligands based on bidentate and tridentate ligands.

The design of bridging ligands is important in regulating the conformation of coordination polymers. Controlling the angle and distance between exo-ligands in the bridging ligands can provide an ordered conformation. We prepared new chiral bridging ligands (*R*)- and (*S*)-**2**, in which two 2,2′:6′,2″-terpyridine (tpy) exo-ligands are linked at 6- and 6′-positions by a chiral binaphthyl spacer. Single-stranded helical coordination polymers could be formed by using twisted bis-tridentate exo ligands and metal ions that adopt octahedral coordination geometry. Moreover, the optically active spacer provides a bias in the twist sense of the helical structures. Herein we report the self-assembly of chiral bridging ligands to stereospecific helical coordination polymers. The angles, locations, and distances among metal centers could be controlled by using these twisted bridging ligands. We selected iron(II) as the metal ion for self-assembling of bridging ligands because of its formation of thermodynamically stable complexes with tpy.[4]

A pair of enantiomeric bridging ligands (*R*)- and (*S*)-**2** were prepared enantioselectively from (*R*)- or (*S*)-1,1′-binaphthol (commercially available, >99% ee). In this study, optically active (*R*)- and (*S*)-1,1′-binaphthol were chosen as starting materials because their optical stability has been well studied and they produce a strong chiral field.[5] The twisted bridging ligands (*R*)- and (*S*)-**2** having C_2 symmetry were synthesized from 1-(2-pyridylcarbonylmethyl)pyridinium iodide and **1**[6] in 42% overall yield (Scheme 1). All products were characterized by FT-IR, ^{1}H NMR, HPLC, and mass spectrometry (see Supporting Information). The ligands exhibited equal and opposite optical rotations in THF ((*R*)-**2**, $[\alpha]_D$ −168.5°; (*S*)-**2**, $[\alpha]_D$ +168.2°).

To investigate the possibility of assembly between (*R*)-**2** and Fe^{2+}, the absorption spectra were monitored for varying concentrations of Fe^{2+} ion in the $CHCl_3$−methanol solution (1:1 v/v) (Figure 1). The absorption spectrum of (*R*)-**2** changed after the addition of Fe^{2+} ion to the bridging ligand solution, and a metal-to-ligand charge transfer (MLCT) band appeared at 576 nm.[7] The maximum absorbance at 576 nm was observed to be approximately proportional to the bridging ligand concentration as shown in the inset of Figure 1. The titration study provided strong evidence of the formation of octahedral $Fe(tpy)_2$ complex between two tpy ligands and one Fe^{2+}, and the twisted bridging ligand (*R*)-**2** was assembled into the polynuclear complex.

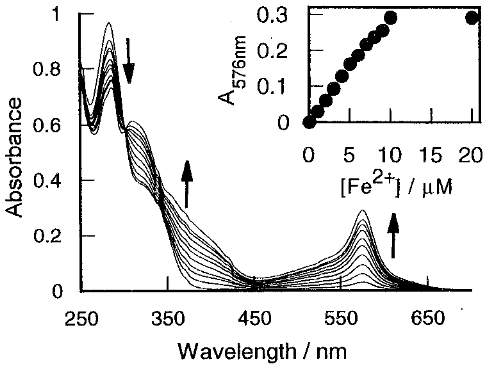
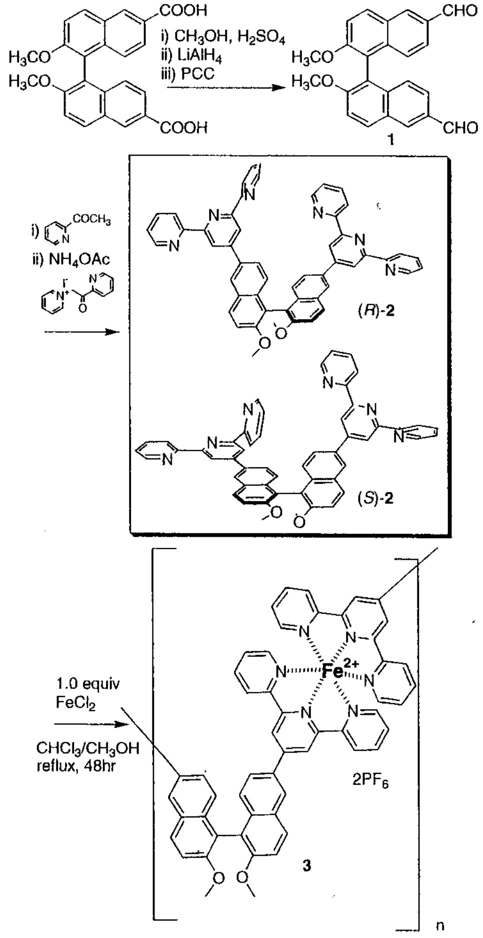


Figure 1. Effect of Fe^{2+} concentration on the absorption spectra of (*R*)-**2** (10μM) in chloroform−methanol: $[Fe^{2+}]$ = 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 μM. Arrows indicate the direction of the spectral change. The inset shows the relationship between Fe^{2+} concentration and the absorbance at 576 nm.

Scheme 1



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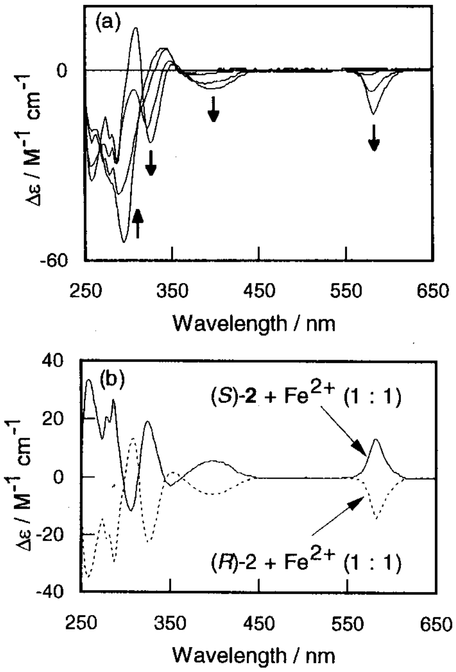
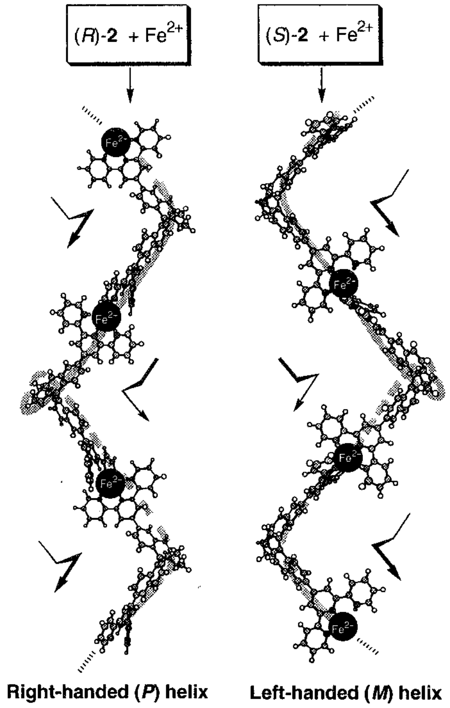


Figure 2. (a) Effect of Fe^{2+} concentration on the CD spectra of (*R*)-**2** (0.1 mM) in $CHCl_3$−methanol at 20 °C: $[Fe^{2+}] = 0$, 0.02, 0.06, 0.1 mM. Arrows indicate the spectral change. (b) Circular dichroism spectra of (*R*)- (···) and (*S*)-**2** (—) (0.1 mM) in the presence of Fe^{2+} (0.1 mM).

A chiral structure was expected from the formation of a polynuclear complex between the chiral bridging ligand and Fe^{2+}. The circular dichroism (CD) spectrum provided the structural information on the chiral structure. Figure 2 shows the CD spectral changes of (*R*)-**2** from the addition of Fe^{2+} in chloroform−methanol (1:1 v/v). The fact that the observed CD spectrum only reveals ligand (*R*)-**2** is due to the chiral binaphthyl spacer. The magnitude of the negative CD signal at the MLCT band ($\Delta\epsilon_{576}$) decreased as Fe^{2+} concentration increased and saturated at the same concentration of (*R*)-**2** ($\Delta\epsilon_{576} = -13$ M^{-1} cm^{-1}). The induced CD in the MLCT band indicated the formation of an asymmetric field surrounding the optically inactive $Fe(tpy)_2$. Furthermore, a new peak appeared at 324 nm ($\Delta\epsilon_{324} = -23$ M^{-1} cm^{-1}), and a significant Cotton effect was exhibited at approximately 310 nm. The opposite response of the CD spectra was observed in (*S*)-**2** and Fe^{2+}, indicating the opposite helical sense. Constable et al. have reported the assignment of *P* and *M* helical sense of diastereoselective dicopper double helicates by CD sign at 320 nm.[3,8] The CD spectra of stereospecific helical polymers containing chiral binaphthyl units have also been reported by several groups.[9] In the current study, the shape of the observed CD spectrum suggested that the chiral bridging ligands (*R*)-**2** and (*S*)-**2** were assembled into the *P* and *M* optically active helical structures, respectively (Scheme 2).

The coordination polymer **3** was prepared by polymerization between (*R*)-**2** and $FeCl_2$ in $CHCl_3$−methanol solution (see Supporting Information). The polymer **3** precipitated as purple material and was soluble in many organic solvents (e.g., acetone, CH_3CN, and DMF) but not water, methanol, or $CHCl_3$. The UV−vis and CD spectra of the isolated **3** were similar to the spectra observed in the titration study. The molecular weight (M_n) and polydispersity (M_w/M_n) were estimated to be 7.0×10^4 and 1.48 by gel permeation chromatography (GPC). For **3** with a molecular mass per repeat unit of 1122.2, this value of M_n corresponds to 50 repeated units. ^1H NMR spectrum of **3** in CD_3CN did not contain any peak of the free ligands as end groups. The intrinsic viscosity $[\eta]$ of **3** was 26 mL/g in CH_3CN at 25 °C.[10] The lack of peaks for free ligands in ^1H NMR as well as the η value also implied a high degree of polymerization. The matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI−TOF−MS) gave only the fragment $[Fe((R)\text{-}\mathbf{2})_2](PF_6)_2$, in which no peak corresponding to the cyclic oligonuclear complex was detected.[9] Therefore, the combination of the chiral bridging ligand (*R*)-**2** and Fe^{2+} formed a soluble high-molecular-weight helical coordination polymer through coordination bonds. Electrochemical studies of **3** in dry CH_3CN solution containing 0.1 M $(TBA)PF_6$ as the supporting electrolyte were performed. Cyclic voltammograms of **3** showed the characteristics of a reversible one-electron oxidation at +0.80V vs Fc/Fc^+.[10] This reversible oxidation process corresponds to an Fe^{2+}/Fe^{3+} couple. This result indicates that the iron centers in **3** are electrochemically equivalent and oxidizable at the same potential.

Scheme 2. Schematic Representation of Stereospecific Assemblies of Chiral Bridging Ligands (*R*)- and (*S*)-2



In conclusion, we have demonstrated the stereospecific formation of high-molecular-weight *P* or *M* helical coordination polymers through the self-assembling process between the twisted bridging ligand and Fe^{2+} ion. The multielectron redox reaction in these helical coordination polymers may prove useful for developing effective asymmetric catalytic systems.

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Supporting Information Available: Experimental procedures and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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