Research Letter

The Studies of Conditions for Inducing Chirality to Cu(II) Complexes by Chiral Zn(II) and Ni(II) Complexes with Schiff Base

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Recently, we have discovered that some chiral Schiff-base nickel(II) complexes induced d-d bands of CD spectra of some achiral copper(II) complexes. However, the novel phenomenon could be observed only a few systems of hybrid materials or limited conditions so far. In order to test conditions about copper(II) ions, we investigated model systems (1) metal-dendrimer (Cu-PAMAM; G4-NH₂ terminal) containing relatively small amount of copper(II) ions (4.5 equivalent to PAMAM) for modeling separated systems of achiral copper(II) complex from chiral Schiff-base nickel(II) or zinc(II) complexes, Bis(*N*-*R*-1-naphtylethyl-3,5-dichlorosalicydenaminato)nickel(II) or zinc(II) by polymer matrix. (2) equilibrium of copper(II) *N*-ethylethylenediamine complexes to measure absorption spectra of d-d band, pH, and electron conductivity during titration of copper(II) ions. The results showed that (1) 4.5Cu-PAMAM could not be induced their d-d bands by the chiral nickel(II) or zinc(II) complexes, which suggested that separation by polymers prevented from inducing CD peaks. (2) Although 36Cu-PAMAM was known, uncoordinated copper(II) ions excess to ligands mainly attributed to increase electron conductivity by remained ions in methanol solutions, which was not associated with intermolecular interaction or dipole moments being effective for the induced CD mechanism by using molecular recognition between neutral molecules of metal complexes.

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1. Introduction

In recent years, various types of organic/inorganic hybrid materials have been studied, for example, organic part of photochromic compounds working as photoswitching moiety and inorganic part of metal compounds working as functional moiety for electronic properties (e.g., magnetic and redox catalytic) or molecular shapes (e.g., stereochemical and conformational). By employing transition metal complexes as inorganic parts in such systems, we have developed supramolecular hybrid materials containing photochromic compounds and chiral Schiff-base metal complexes [1–3]. Accompanying with photoisomerization of azobenzene or its derivatives, chiral Schiff-base ligands of nickel(II), copper(II), and zinc(II) complexes changed their conformation in solutions of organic solvents (methanol, chloroform, acetone, *N,N'*-dimethylformamide, and toluene), which could be detected by CD spectroscopy as well as absorption electronic spectra. Moreover, their spectral features (solvatochromism) and degree of smooth conformational changes

are also different depending on solvents. Suitable groups of azobenzenes or Schiff-base ligands [4] suggest that the mechanism of photocontrolling of molecular conformation of supramolecular hybrid systems may be related to a certain intermolecular interactions between solutes. Therefore, we are also interested in other methods to evaluate intermolecular interactions by (absorption electronic, CD, or related) spectroscopy.

In this context, we have discovered that some chiral Schiff-base nickel(II) complexes induced d-d bands of CD spectra at 450, 550, and 650 nm assigned to be d-d transitions of several achiral copper(II) Schiff-base complexes [5]. However, the novel phenomenon could be observed only a few systems of hybrid materials or limited conditions at present. In previous attempt [5], bis(*N*-*R*-1-phenylethyl-3,5-dichlorosalicydenaminato)nickel(II) was only effective chiral complex, while bis(*N*-*R*-1-naphtylethyl-3,5-dichlorosalicydenaminato)nickel(II) was inactive for inducing CD peaks. In view of dipole moment of molecules, large (naphtyl) groups or charged metal ions having

FIGURE 1: Molecular structure of chiral complexes (M = Ni for **1**, M = Zn for **2**). Reference [1].

unpaired electrons seemed to have advantage for inducing CD, albeit actually molecular recognition was also necessary as one of the conditions. Secondly, as employing labile copper(II) complexes, the effects of uncoordinated (solvated) copper(II) ions by dissociation can be expected to exhibit d-d bands in the region corresponding to copper(II) complexes. To confirm the possibility, we should know some properties of copper(II) ions during stepwise titration and formation of complexes being appropriate for inducing such CD bands. Finally, it was observed only in solutions of some organic solvents containing hybrid solutes, while even bis(*N*-*R*-1-naphthylethyl-3,5-dichlorosalicydenaminato)nickel(II) exhibiting larger dipole moment could not induce such CD peaks of the achiral copper(II) complexes in polymer matrix. That induced CD peaks also occur in separated systems via long-range force may be important for understanding the mechanism. To reveal this question, we intended to examine other model systems.

In this paper, we investigated by using model systems (1) metal-dendrimer (Cu-PAMAM, G4-NH₂ terminal) containing relatively small amount of copper(II) ions (4.5 equivalent to PAMAM, abbreviated as 4.5Cu-PAMAM, etc.) for modeling separated systems of achiral copper(II) complex from chiral Schiff-base nickel(II) or zinc(II) complexes, bis(*N*-*R*-1-naphthylethyl-3,5-dichlorosalicydenaminato)nickel(II), or zinc(II) by polymer matrix. (2) Equilibrium of copper(II) *N*-ethylethylenediamine complexes to measure absorption spectra of d-d band around 800 nm, pH, and electron conductivity. The main aim of this study is accumulating new knowledge about this kind of supramolecular hybrid materials.

2. Experimental Section

2.1. Materials. Chemicals and solvents of the highest commercial grade available (3,5-dichlorosalicylaldehyde from TCI; other ones from Wako) were used as received without further purification.

2.2. Sample Preparation. Bis(*N*-*R*-1-naphthylethyl-3,5-dichlorosalicydenaminato) nickel(II) (**1**) or zinc(II) (**2**) (Figure 1) were prepared according to literature [1].

FIGURE 2: Absorption and CD spectra of 4.5Cu-PAMAM and **1** in 0.1 mM methanol solutions.

To 10 mL of 10 wt% methanol solution of G4-NH₂ terminal PAMAM dendrimer (0.029 mM), 2.14 mL of methanol solution of CuSO₄ (0.60 mM) was added according to literature [6] and monitoring by UV-Vis absorption spectra. The 4.5 equivalent amount of copper(II) ions into the interior of the PAMAM dendrimer (4.5Cu-PAPAM) was used for the experiments of induced CD mixed (about 0.1 mM) methanol solution with chiral complexes **1** or **2**.

To 10 mL methanol solution of *N*-Ethylethylenediamine (10 mM), methanol solution of Cu(NO₃)₂·2H₂O (2.5 mM) was added by 1.0 mL dropwise up to 20.0 mL during the titration, we measured UV-vis absorption spectra, pH, and electron conductivity every 1.0 mL addition.

2.3. Physical Measurements. Absorption spectra were measured on a JASCO V-570 UV/VIS/NIR spectrophotometer in the range of 900–200 nm at 298 K. CD (circular dichroism) spectra were measured on a JASCO J-820 spectrophotometer in the range of 900–200 nm at 298 K. The pH was measured with a Mettler Toledo MI229. The electron conductivity was measured with a TOA DK CM-30G.

3. Results and Discussions

Figures 2 and 3 show absorption and CD spectra of 4.5Cu-PAMAM and **1** and **2** in 0.1 mM methanol solutions, respectively. The assignment of bands for **1** and **2** [1] and absorption spectra of stepwise complexation of copper(II) ions into PAMAM has been reported elsewhere [6, 7].

As for a Cu-PAMAM complex, a broad d-d band was observed around 600 nm, intense while LMCT band was observed around 300 nm (not shown) [6]. The intensity of d-d band was proportional to the amount of copper(II) ions coordinated to PAMAM, and dissociated copper(II) ion, namely, formation of solvated copper(II) complexes, resulted

FIGURE 3: Absorption and CD spectra of 4.5Cu-PAMAM and 2 in 0.1 mM methanol solutions.

in shift of peak wavelength. In Figure 2, intense and broad d-d bands of 4.5Cu-PAMAM and weak d-d bands of 1 appeared around 600 nm, respectively.

Of course both achiral PAMAM dendrimer and achiral Cu-PAMAM complexes are inactive for CD spectroscopy, CD peaks are attributed to chiral complexes 1 and 2 mainly. Because nickel(II) or zinc(II) complexes show weak or no d-d bands, predominant absorption and CD peaks below 400 nm are assigned to $\pi-\pi^*$ bonds of chiral Schiff-base ligands. It should be noted that the difference of calculated sum of CD spectra for 4.5Cu-PMMA and 1 or 2 and experimental spectra of mixed solution of 4.5Cu-PMMA and 1 or 2 (in addition, wavelength is d-d or CT band region for the corresponding achiral copper(II) complex) can be ascribed to induced CD peaks by chiral complexes.

In the present case, both 1 and 2 showed no or very slight induced d-d bands of 4.5Cu-PAMAM in 0.1 mM methanol solution (considerably weaker than general intensity values of "observed" ones). Previously, we reported that bis(*N*-*R*-1-naphthylethyl-3,5-dichlorosalicydenaminato) nickel(II) could induce CD peaks of achiral mononuclear Schiff-base copper(II) complexes [8, 9] in more diluted 0.01 mM methanol solutions [5]. Therefore, the reasons for the absence of induced CD peaks for the present cases may be attributed to (1) inappropriate molecular recognition between chiral and achiral metal complexes, indeed the present systems copper(II) ions may exist deeply inner region of PAMAM dendrimers (2) copper(II) ions does not coordinate to PAMAM appropriately, which can be proved to show free copper(II) ions can enhance such induced CD peaks or not.

The possibility of (1) can be supported by these facts; in previous study, induced CD phenomenon exhibited concentration dependence, and suitable combinations about molecular recognition (against expectation by dipole moments of molecules) for several cases. Moreover, induced CD

FIGURE 4: Absorption spectra of 2.5 mM methanol solution of $[\text{Cu}(\text{NO}_3)_2]$ and gradual changes by copper(II) ion titration added every 1.0 mL in 0.1 mM *N*-ethylethylenediamine methanol solutions.

FIGURE 5: Electron conductivity (right; empty squares) and pH (left; filled circle) of copper(II) titration (the $[\text{Cu}(\text{NO}_3)_2]$ solution) in 0.1 mM *N*-ethylethylenediamine methanol solutions.

peaks disappeared by separation of complexes in polymer matrix. Therefore, if the induction is attributed to long-range intermolecular interactions, there are suitable conditions for this system about supramolecular chirality [10, 11].

The possibility of (2) can be confirmed as shown in Figures 4 and 5. As known well, Cu-PAMAM of proper ratio is stable to measure ESR spectra [12, 13] or discuss photochemical reactions [14] generally.

Figure 4 shows absorption spectra of copper(II) ion titration in 0.1 mM *N*-ethylethylenediamine methanol solutions. The peak of d-d bands of pure $\text{Cu}(\text{NO}_3)_2$ solution (excess copper(II) ion in methanol) and that of appropriately complexing species of *N*-ethylethylenediamine (and that of Cu-PAMAM) are apparently different from each other. However, similar study on equilibrium has been reported for the analogous ethylenediamine complexes [15] because it is typical and well-known chelating reagent for copper(II) ion.

The corresponding pH and electron conductivity are shown in Figure 5. Regardless of equilibrium involving protons in solutions [15], the pH values were kept almost constant values if excess copper(II) ions were not contained (below about 5 mL). On the other hand, electron conductivity obviously increased when copper(II) ions were added more than equivalent ratios.

The features suggest that excess or dissociated free copper(II) ions give rise to solvated species, which exhibit

shifted d-d bands Cu-PAMAM at least distinguishable. Free copper(II) ions contained in solution systems may result in slight changes in pH and increasing of electron conductivity, which may be increasing polarity of the solutions. However, the magnitude of increasing polarity may be less than that of solvatochromism of different organic solvents.

4. Conclusions

The present results showed that (1) the 4.5Cu-PAMAM could not be induced their d-d bands by the chiral Schiff-base nickel(II) or zinc(II) complexes, which suggested that separation by polymers prevented from inducing CD peaks. (2) Although even 36Cu-PAMAM was known, uncoordinated copper(II) ions excess to ligands mainly attributed to increasing electron conductivity by remained ions in methanol solutions, which was not associated with intermolecular interaction or dipole moments effective for the induced CD mechanism by using molecular recognition between neutral molecules.

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References

- [1] T. Akitsu, "Photofunctional supramolecular solution systems of chiral Schiff base nickel(II), copper(II), and zinc(II) complexes and photochromic azobenzenes," *Polyhedron*, vol. 26, no. 12, pp. 2527–2535, 2007.
- [2] T. Akitsu and Y. Einaga, "Synthesis, crystal structures and electronic properties of Schiff base nickel (II) complexes: towards solvatochromism induced by a photochromic solute," *Polyhedron*, vol. 24, no. 14, pp. 1869–1877, 2005.
- [3] T. Akitsu and Y. Einaga, "Syntheses, crystal structures and electronic properties of a series of copper(II) complexes with 3,5-halogen-substituted Schiff base ligands and their solutions," *Polyhedron*, vol. 24, no. 18, pp. 2933–2943, 2005.
- [4] T. Akitsu and Y. Einaga, "Bis[(R)-3,5-dichloro-N-(1-phenylethyl)salicylideneaminato- κ^2N, O]-copper(II) and bis[(R)-3-ethoxy-N-(1-phenylethyl)salicylideneaminato- κ^2N, O]-copper(II)," *Acta Crystallographica Section C*, vol. 60, part 12, pp. m640–m642, 2004.
- [5] T. Akitsu, N. Uchida, Y. Aritake, and J. Yamaguchi, "Induced d-d bands in CD spectra due to chiral transfer from chiral nickel(II) complexes to achiral copper(II) complexes and application for structural estimation," *Trends in Inorganic Chemistry*. In press.
- [6] M. Zhao, L. Sun, and R. M. Crooks, "Preparation of Cu nanoclusters within dendrimer templates," *Journal of the American Chemical Society*, vol. 120, no. 9, pp. 4877–4878, 1998.
- [7] R. M. Crooks, M. Zhao, L. Sun, V. Chechik, and L. K. Yeung, "Dendrimer-encapsulated metal nanoparticles: synthesis, characterization, and applications to catalysis," *Accounts of Chemical Research*, vol. 34, no. 3, pp. 181–190, 2001.
- [8] T. Akitsu and Y. Einaga, "Bis[2-(quinolin-3-yliminomethyl)phenolato- κ^2N, O]-copper(II)," *Acta Crystallographica Section E*, vol. 60, part 11, pp. m1552–m1554, 2004.
- [9] T. Akitsu and Y. Einaga, "Bis[2-(phenethyliminomethyl)phenolato- κ^2N, O]-copper(II)," *Acta Crystallographica Section E*, vol. 60, part 11, pp. m1555–m1557, 2004.
- [10] V. V. Borovkov, G. A. Hembury, and Y. Inoue, "Origin, control, and application of supramolecular chirogenesis in bisporphyrin-based systems," *Accounts of Chemical Research*, vol. 37, no. 7, pp. 449–459, 2004.
- [11] G. A. Hembury, V. V. Borovkov, and Y. Inoue, "Chirality-sensing supramolecular systems," *Chemical Reviews*, vol. 108, no. 1, pp. 1–73, 2008.
- [12] M. F. Ottaviani, S. Bossmann, N. J. Turro, and D. A. Tomalia, "Characterization of starburst dendrimers by the EPR technique. 1. Copper complexes in water solution," *Journal of the American Chemical Society*, vol. 116, no. 2, pp. 661–671, 1994.
- [13] M. F. Ottaviani, F. Montalti, N. J. Turro, and D. A. Tomalia, "Characterization of starburst dendrimers by the EPR technique. Copper(II) ions binding full-generation dendrimers," *The Journal of Physical Chemistry B*, vol. 101, no. 2, pp. 158–166, 1997.
- [14] H. Wan, S. Li, T. A. Konovalova, S. F. Shuler, D. A. Dixon, and S. C. Street, "Experimental and theoretical studies of the photoreduction of copper(II)-dendrimer complexes," *Journal of Physical Chemistry C*, vol. 112, no. 5, pp. 1335–1344, 2008.
- [15] R. Zingales, "Chemical equilibria involving copper(II) ethylenediamine complexes," *Journal of Chemical Education*, vol. 80, no. 5, pp. 535–536, 2003.