

**THE STUDIES OF CONDITIONS FOR INDUCING  
CHIRALITY OF SUPRAMOLECULAR  
SELF-ASSEMBLIES OF (CHIRAL)  
Cu(II) COMPLEXES AND  
PHOSPHOLIPIDS**

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**Abstract**

We have attempted to observe induced CD bands for supramolecular assemblies composed of typical (chiral) copper(II) complexes incorporating amino acid ligands (alanine and glycine, abbreviated as **Cu-ala** and **Cu-gly**, respectively) and typical chiral phospholipid, lecithin derivative (abbreviated as **PL**). It is a well-known biomaterial to form vesicles of lipid bilayers by self-assembly process. Although, we could measure normal CD spectra of the chiral copper(II) complex, whose absolute structures were also confirmed by X-ray crystallography before using the experiments, aqueous solutions of **Cu-ala** and **PL** or **Cu-gly** and **PL** did not appear expected CD bands. By comparing with other systems of our previous studies on chiral metal complexes exhibiting induced CD phenomenon, we discuss suitable conditions (or investigating causes of failure according to the aims and scopes of this journal) for these systems.

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Keywords and phrases: chirality, copper(II) complexes, phospholipids, alanine, glycine.

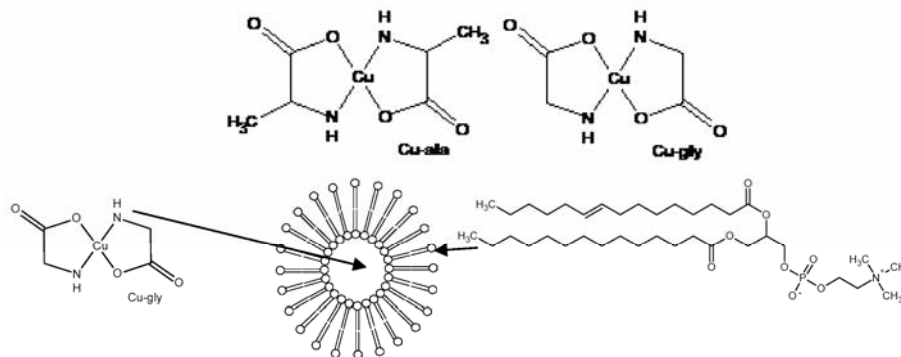
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## 1. Introduction

Besides classical treatment of biochemistry, chirality may also be one of the most important concepts for many new fields of chemistry, for example, coordination compounds as organic/inorganic hybrid materials (Mason [12], Amouri and Gruselle [8]), nano-scaled materials (Amabilino [7]), and supramolecular chemistry (Borovkov et al. [9], Hembury et al. [11]). Among them, “chiral transfer” between metal complexes (Crassous [10]) is challenging approach to develop new molecule-based functional materials. In this context, we have investigated co-crystals of chiral cyanide-bridged bimetallic assemblies (Akitsu [2], Akitsu et al. [3]) and chiral double salts connected with electrostatic interaction in crystals (Akitsu and Einaga [1]). In a chiral crystal, CD bands in the region of (achiral) cyanide moieties can be observed as intense charge transfer bands.

Furthermore, not only solid state, but also mixed solutions have been investigated, for example, (1) chiral Schiff base complex---(chiral) Schiff base complex (Akitsu et al. [5]), (2) chiral Schiff base complex---ferrocene (Akitsu and Uchida [6]), and (3) chiral Schiff base complex---metallodendrimer or metal cluster (Akitsu et al. [4], Akitsu et al. [5]). However, conditions for inducing CD by chiral Schiff base complexes are limited for each case. The systems of (1), (2), and (3) are mainly limited by bulky steric factors chiral ligands, kinds of both chiral ligands metal ions (coordination environment), and amount of coordinated metal ions in dendrimers, respectively. In particular, it is proved that, separation by large organic dendrimers may be bad conditions (appropriate ratios of copper(II) ion for coordination to G4-PAMAM dendrimers is also important) for inducing chirality for the case of (3).

Herein, we attempted to develop to nano-scaled biochemical organic/inorganic hybrid supramolecular assemblies composed of typical copper(II) complexes incorporating amino acid ligands (alanine and glycine, abbreviated as **Cu-ala** and **Cu-gly**, respectively; Figure 1) and typical phospholipid, lecithin derivative (**PL**).

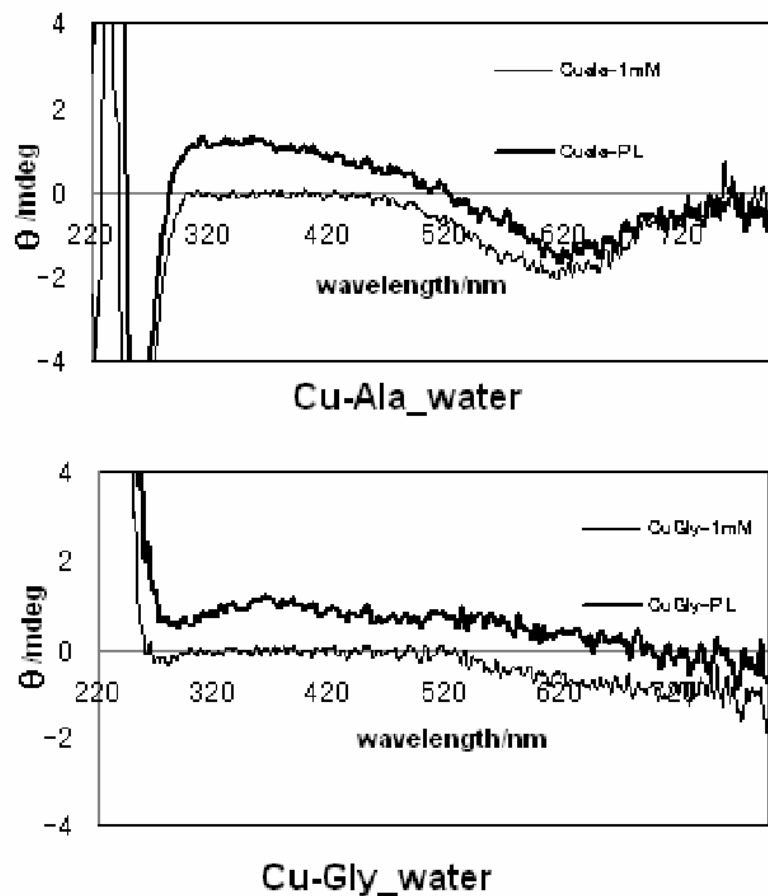


**Figure 1.** Structures of **Cu-ala** and **Cu-gly** and a proposed structure of supramolecular assembly **Cu-gly-PL**.

Lecithin derivative was purchased commercially and used without further purification and copper(II) complexes with amino acids, **Cu-ala** (Yasui [14]) and **Cu-gly** (Mauthner [13]), were prepared according to the literature procedures. Structure of **Cu-ala** and **Cu-gly** was also confirmed (by Flack parameters for **Cu-ala**) with *X*-ray crystallography before using experiments completely. By mixing **Cu-ala** (or **gly**) and **PL** in 1mM aqueous solutions at room temperature, we have prepared supramolecular assemblies **Cu-ala** (or **gly**)-**PL** by self-assembly process (Figure 1).

Figure 2 exhibits CD spectra of aqueous solutions of **Cu-ala** and **Cu-ala-PL** and **Cu-gly** and **Cu-gly-PL**. For **Cu-ala-PL**, a characteristic d-d band due to **Cu-ala** was observed around 620nm with slightly decreasing of its band width. On the other hand, for **Cu-gly-PL**, spectral difference between only **Cu-gly** and **Cu-gly-PL** are not clear. Though **PL** is also a chiral compound without absorption band around 500-900nm, induced CD or at least some effects caused by mixing of copper(II) complexes, and **PL** depends on not only concentration but also self-assembling features.

In conclusion, we have indicated that *structures of self-assemblies* must be one of the most important factors or conditions for inducing CD of these supramolecular systems.



**Figure 2.** CD spectra of aqueous solutions of [Cu-Ala<sub>water</sub>] **Cu-ala** (thin line) and **Cu-ala-PL** (bold line) and [Cu-Gly<sub>water</sub>] **Cu-gly** (thin line) and **Cu-gly-PL** (bold line).

### References

- [1] T. Akitsu and Y. Einaga, Asian Chem. Lett. 10 (2006), 103.
- [2] T. Akitsu, Syntheses, structure, and electronic properties of assemblies of diastereomers of nickel (II) complexes with tetracyanometalates  $[M(CN)_4]^{2-}$  ( $M = Ni, Pd, \text{ and } Pt$ ), in Stereochemistry Research Trends, Nova Science Publishers, Inc.(NY, USA), Chapter 4 (2008), 107-128.
- [3] T. Akitsu, Y. Einaga and K. Yoza, Open, Inorg. Chem. J. 2 (2008), 1.

- [4] T. Akitsu, J. Yamaguchi, N. Uchida and Y. Aritake, *Res. Lett. Mater. Sci.* 484172 (4 pages) (2009).
- [5] T. Akitsu, J. Yamaguchi, Y. Aritake, T. Hiratsuka and N. Uchida, *Int. J. Curr. Chem.* 1 (2010), 1.
- [6] T. Akitsu and N. Uchida, *Asian Chem. Lett.* 14 (2010), 21.
- [7] D. B. Amabilino, *Chirality at the Nanoscale*, Wiley-VCH, Weinheim, (2009).
- [8] H. Amouri and M. Gruselle, *Chirality in Transition Metal Chemistry*, John Wiley and Sons Ltd., West Sussex, (2008).
- [9] V. V. Borovkov, G. A. Hembury and Y. Inoue, *Acc. Chem. Res.* 37 (2004), 449.
- [10] J. Crassous, *Chem. Soc. Rev.* 38 (2009), 830, and references therein.
- [11] G. A. Hembury, V. V. Borovkov and Y. Inoue, *Chem. Rev.* 108 (2008), 1.
- [12] S. F. Mason, *Molecular Optical Activity & the Chiral Discriminations*, Cambridge University Press, Cambridge, (1982 & 2009).
- [13] J. Mauthner and W. Suida, *Monatsh.* 11 (1890), 373.
- [14] T. Yasui, *Bull. Chem. Soc. Jpn.* 38 (1965), 1746.

