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Review

Application of the ΔΛ isomerism of octahedral metal complexes as a chiral source in photochemistry

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Abstract

Photochemical studies on the use of chiral metal complexes in homogenous and heterogeneous systems are surveyed and commented on their significance. A main focus is laid on the utility of the ΔΛ isomerism of octahedral metal complexes as a chiral source. The reported works demonstrate that chiral metal complexes are effective as a molecular element in achieving varieties of functions such as chiral discrimination, chiral transfer, sensing and photoresponsive guests for biomolecules or liquid crystals.

Keywords: Chiral metal complexes; ΔΛ isomerism; Photochemistry; Photosensitizer; Photooxidation; Asymmetric reaction; Catalysis; Chiral sensor; Fluorescence; Clay minerals; DNA; Monolayer; Liquid crystal; Azo compounds; Photoracemization; Photoisomerization; Cyclodextrin; Sulfide

Contents

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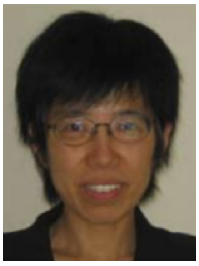


Hisako Sato was born in Ehime, Japan. She received B.S. degree in Applied Chemistry from Waseda University, Tokyo, Japan, 1981, the M.S. degree in Chemistry from the University of Tokyo, Tokyo, Japan, in 1983, the Ph.D. degree from Hokkaido University, Hokkaido, Japan, in 1992, the Ph.D. degree from the University of Tokyo, Tokyo. Japan, in 1999. In 1983, she joined Hitachi Ltd., Tokyo, Japan. She engaged in silicon device modeling for VLSI design. In 2002, she joined the University of Tokyo as a research fellow. From 2003 to 2006, she has been CREST researcher by JST. She engaged in theoretical study and the application of inorganic nanosheet for sensor and device. Since 2006, she has been named the PRESTO project leader sponsored by JST. Her current interest is to develop the two-dimensional chiral networks of metal complexes by use of chemical reactions at an air–water interface for molecular devices based on chirality.

Akihiko Yamagishi was born in Chiba in 1943. He received B.S. (Chemistry), 1967, M.S. (Chemistry), 1969 and D.Sc. (Chemistry), 1975 from The University of Tokyo. From 1970 to 1985, he was research associate, the College of Science, Hokkaido University. From 1976 to 1978, he was a post-doctoral fellow, the State University of New York at Syracuse under the instruction of Professor Michael Szwarc. From 1985 to 1991, he was associate professor, the College of Arts and Sciences, The University of Tokyo. From 1991, he was professor in the Department of Science, Hokkaido University. From 2001 to 2006, he was professor in the Graduate School of Science, The University of Tokyo. From 2006, he has been Visiting processor in the Faculty of Science, Ochanomizu University. His research field is Clay Science, Inorganic Science, and Surface Science. His main interest is the interaction of inorganic layered compounds with metal complexes or organic compounds with a focus on the role of chirality in molecular recognition. He was prized 1986 the CSJ Award for Creative Work from the Chemical Society of Japan and 1999 the Clay Science Society of Japan Award. He was President of the Clay Mineral Society of Japan from 2002 to 2004.

1. Introduction

Since the discovery by Alfred Werner in the late century, the chirality of metal complexes has been attracting a continuing interest in the field of coordination chemistry [1–4]. Chiral metal complexes are employed in both fundamental and practical areas as catalysts, sensors and electronic devices [2–8]. The achievement of their functions is manifested in terms of molecular functions such as the discrimination of molecular chirality, the transfer of chirality from one species to another and the amplification of chirality to a supramolecular scale.

There are several structural origins for the chirality of metal complexes as below:

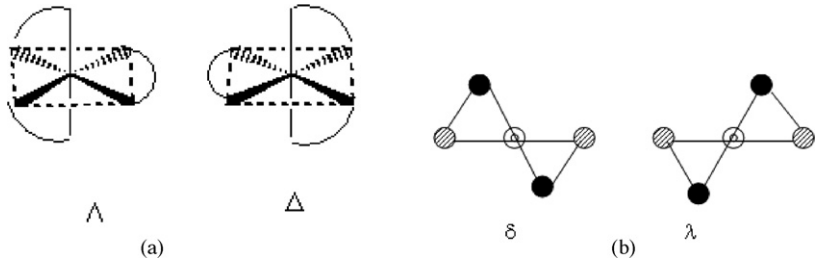
(i) *Chiral coordination structure*: Two vicinal ligands coordinated in a metal complex are possible to take a helical conformation. Tris-chelated octahedral complexes, for example, have Δ- and Λ-chirality, depending on the twisting direction of two ligands as shown in Scheme 1a. This type of chirality is unique in metal complexes.

(ii) *Chiral ligands*: A chiral ligand maintains chirality when it is coordinated to a metal ion. Amino acidato complexes, for example, possess both coordination and ligand chiralities.

(iii) *Chirality induced by coordination*: Some achiral ligands become chiral when they are coordinated to a metal ion due to the fixation of twist conformation. Ethylenediamine, for example, becomes chiral when it is coordinated as a bidentate ligand. This kind of chirality is denoted as δ and λ as shown in Scheme 1b.

Among the above structural origins, the most remarkable features appear as a chiral source in the case of the helical conformation of ligands (i). Such chirality has the following unique characteristics as compared with organic compounds. Firstly the chiral coordination structure of a metal complex is rigid and robust particularly when the coordinated ligands form a chelate ring. The structure suffers from no flexibility since the ligand is fixed at more than two coordination sites. Secondly a large helix appears when the coordinated ligands are planar and bulky. For example, it may extend a few nanometers in case of polypyridyl ligands such as 2,2′-bipyridyl and 1,10-phenanthroline (Scheme 2). Thirdly multi-functionality is achieved when these structural features are coupled with the properties of a central metal ion, particularly in case of transition metals. The chiral nature of a metal complex is even more efficient when it is related to its electronic, magnetic and photophysical properties. By combining chiral structures with photoresponsive properties, for example, metal complexes play a role of photocatalyst in asymmetric reactions. Lastly the systematic variation of detailed properties is possible by including a series of metal ions. A particular nature such as the electron density at some positions of a ligand can be varied systematically by changing a metal ion in the periodic table.

In this review, we report the attempts of asymmetric photochemistry by use of chiral metal complexes in both homogeneous and heterogeneous systems. The reviewed systems cover inorganic, bioorganic hosts, liquid crystals and molecular films. At the last session, the application of sensing systems based on chiral photoresponsive metal complexes incorporated in molecular films is reviewed.



Scheme 1. (a) Δ- and Λ-configurations. (b) Chirality of ethylene diamine: nitrogen atoms (filled circles) and carbon atoms (shadowed circles).