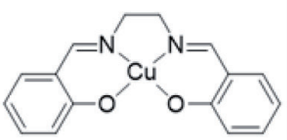
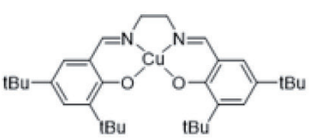
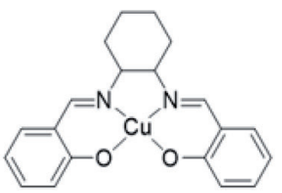
Chapter

Introductory Chapter: Chirality from Molecular Electronic States

Takashiro Akitsu

1. Chiral assembly of proteins and metal complexes

Needless to say, chirality is an important concept along the fields of biology, chemistry, and physics. Not only steric fitness (stereochemical aspects) but also electronic properties (or electronic states as origin) may be important in such cases, which is a motivation to emphasis the concept of this book.

PIFKIY① [1] GOLDScore: 49.8676	MAGSOD② [2] GOLDScore: 53.5195	PAYDEY③ [3] GOLDScore: 23.2850
		
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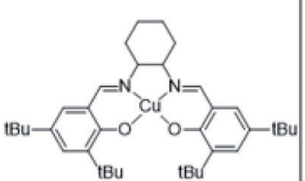
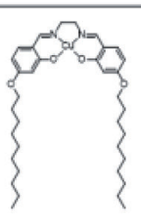
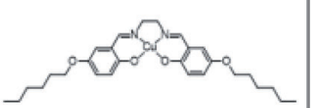
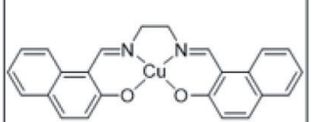
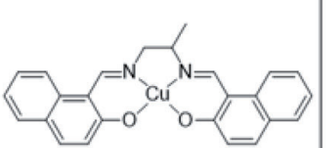
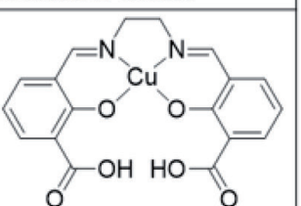
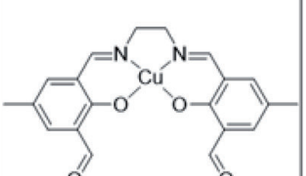
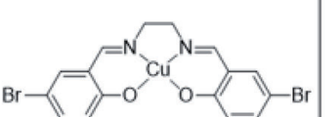
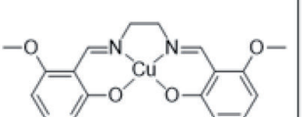
		

ENPCUA [7] GOLDScore: 48.2661	DEMTAR [8] GOLDScore: 64.4997	ENOKUO [9] GOLDScore: 40.3257
		
MOGSOS [10] **GOLDScore: 51.4381**	**FOWCUQ [11]** **GOLDScore: 48.2838**	**ANEMAJ [12]** **GOLDScore: 48.2661**
		

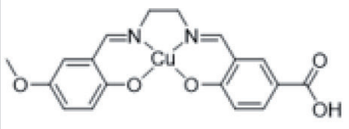
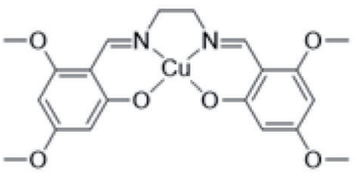
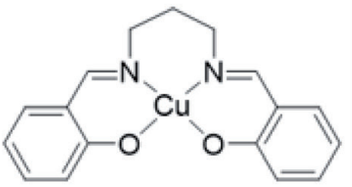
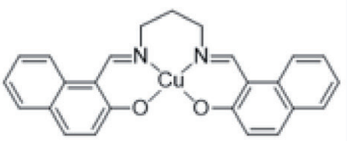
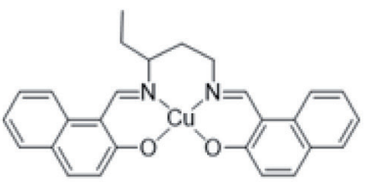
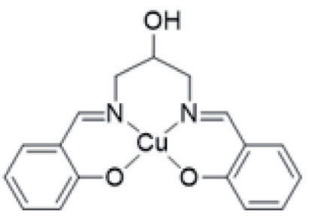
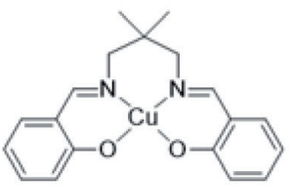
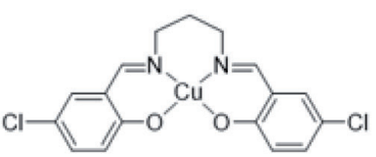
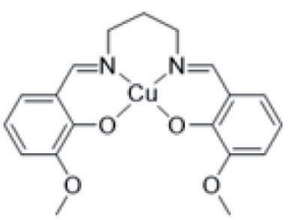
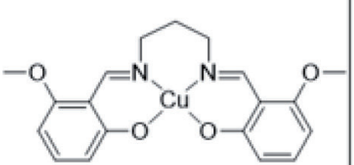
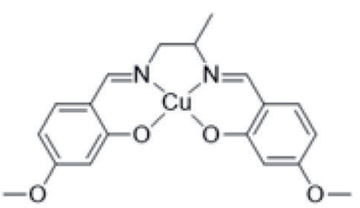
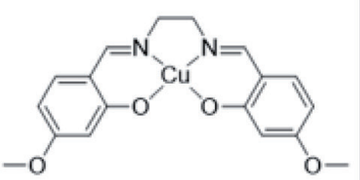
NEXFOM [13] **GOLDScore: 53.7217**	**VUYHUT [14]** **GOLDScore: 51.2235**	**CASUAT [15]** **GOLDScore: 47.3524**
		
BEJSIS [16] **GOLDScore: 55.2314**	**KOQYOG [17]** **GOLDScore: 54.3256**	**DUNPIL [18]** **GOLDScore: 55.4040**
		
QEKDUF [19] **GOLDScore: 34.3787**	**XAXWAU01 [20]** **GOLDScore: 47.0893**	**AJIKOU [21]** **GOLDScore: 58.3212**
		
MIGJUI [22] **GOLDScore: 49.0211**	**ANEMOX [23]** **GOLDScore: 52.4909**	**WICBIU03 [24]** **GOLDScore: 49.7661**
		

Table 1.
GOLD scores of docking copper(II) complexes into lysozyme. Detailed study of the best four complexes will be reported elsewhere.

In recent years, in order to prepare "artificial metalloproteins" composed of natural proteins (typically egg white lysozyme) including synthesized metal complexes (salen-type Cu(II) complexes), we searched and investigated candidate metal complexes using crystal structure databases (CSD [1–24] and PDB). In this context, we used a GOLD program to search well docking features between proteins and ligand of small molecules structurally and obtained docking scores (**Table 1**). As for molecular structures, DFT calculations from a Gaussian 09 program may be useful to obtain not only optimized structures but also detailed electronic states of metal complexes in principle.

At least proteins must be a hard target to discuss. Once I asked to my collaborator of computational chemical physics, "I will ask you DFT calculations of

simulated IR spectra of them. Moreover, I also want to know simulated IR spectra of amide I, II, and some other bands for typical proteins such as lysozyme." Then he replied, "When you'll send me the data, I'll continue with the assignment. I don't know how long do you like the discussion of the vibrational bands, and what are the most interested bands for you. Additionally, strong bands corresponding to intermolecular H-bands appear in the exp. spectrum. If you have the X-ray data of these molecules, I can simulate it and improve the assignments."

Even employing achiral metal complexes, such hybrid assembly must be a chiral material, which can be experimentally elucidated by means of chiroptical spectroscopy (CD or VCD) [25] as well as quenching of fluorescence intensity (obeying Stern-Volmer plot) [26]. However, calculations of electronic state for such hybrid assembly must be difficult only by means of these conventional or commercially available programs at present [27]. In this way, supramolecular chirality may be one of the challenging targets in near future.

2. Chiral metal complexes by spectroscopy, magnetism, and computational interpretation

In the case of chiral salen-type metal complexes, it is not easy to investigate their electronic properties using both experimental and theoretical methods. Previously, we have systematically studied on preparations, crystal structures, and electronic states for mononuclear (3d) [25–27] and binuclear (3d-4f) [28–32] complexes. Besides X-ray crystallography and IR spectra, CD and UV-vis spectra, XAS spectra, fluorescence spectra, and magnetic measurements were used. However, not all

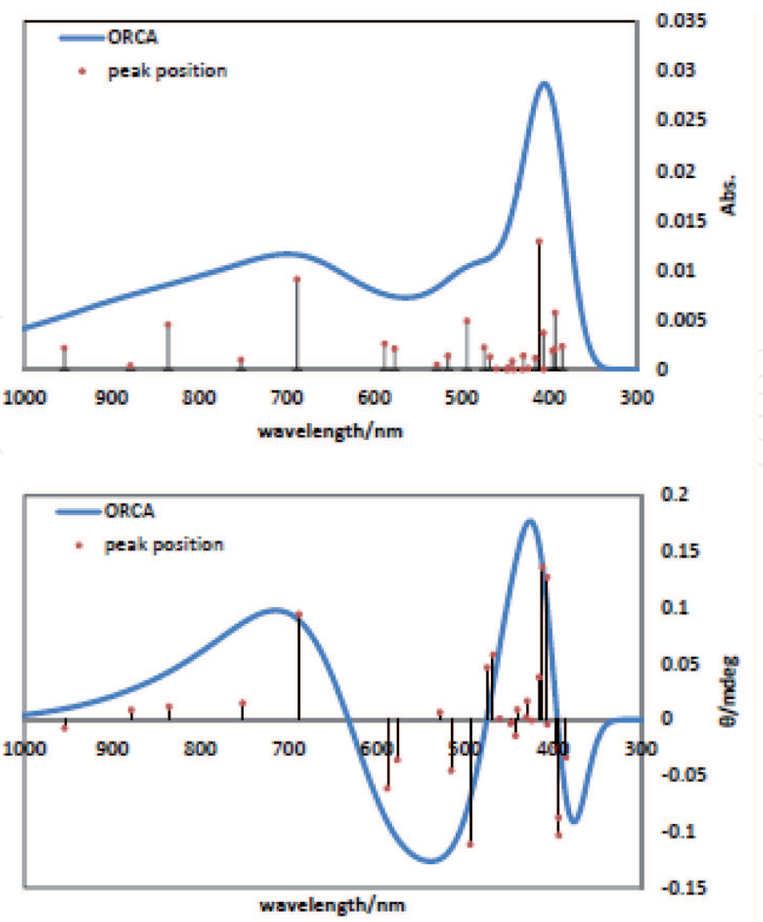


Figure 1.
Simulated UV-vis and CD spectra for La(III)-Cu(II) complex [27].

methods are valid at the same time for one complex of a certain combination of 3d and 4f metal ions, for example, some complexes were diamagnetic, and some complexes did not exhibit emission. Hence, we also carried out DFT or semiempirical molecular orbital calculations as well as these experiments. However, 4f metal ions having many electrons usually took a long time to calculate with DFT accurately and the results often deviated from the corresponding experimental data largely (for example, simulated CD spectrum shown in **Figure 1**).

In conclusion, beyond stereochemical aspects, chirality may be important, though there are limited methods to elucidate their electronic states in particular theoretically such as chiroptical spectra and expanding supramolecular functions at present.

Author details

Takashiro Akitsu
Department of Chemistry, Faculty of Science, Tokyo University of Science, Tokyo, Japan

*Address all correspondence to: akitsu2@rs.tus.ac.jp

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