

## Photoisomerization of azobenzene-containing amino acid derivative Schiff base copper(II) complexes with lysozyme

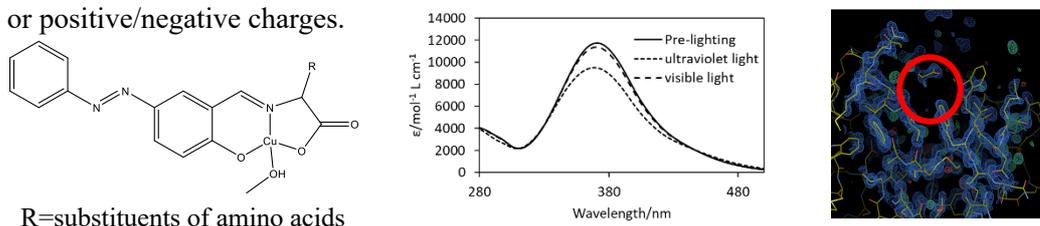
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Study of artificial metalloproteins is an important topic from the viewpoint of functional materials for adding rich functions of metal complexes to native proteins<sup>1</sup>. With respect to photo-switching of biochemical functions of proteins, organic azobenzene derivatives exhibiting photoisomerization have been mainly studied as ligands. However, there have been only a few examples using ligands of metal complexes occurring photoisomerization. Metal complexes can be expected for fine tuning of structural and/or spatial aspects as well as redox properties<sup>2</sup>. In this study, we prepared composites of azobenzene-containing amino acid derivative Schiff base copper(II) complexes and lysozyme to investigate spectroscopic properties due to photoisomerization of azobenzene moiety.

Several new copper(II) complexes were prepared in common procedures [2] using corresponding amino acids (Fig 1. left). Inclusion of the complexes into lysozyme was confirmed by means of UV-vis and fluorescence spectra and discussed by using a protein-ligand docking program GOLD. Photoisomerization of azobenzene due to UV or vis light irradiation was examined for the complexes solely and their composites with lysozyme in phosphate buffer solutions.

Some of the complexes exhibited typical *cis-trans* photoisomerization of azobenzene (Fig. 1 middle). Inclusion with non-covalent nor coordination bonding into lysozyme were suggested by quenching of fluorescence intensity, which was also supported by preliminary crystallographic analysis (around His 15, the most stable site for metal coordination) of single crystals of lysozyme soaking the complexes (Fig. 1 right). Degree of photoisomerization and non-covalent inclusion (or coordination to His15) to lysozyme depended on several kinds of substituent group effects of amino acid moieties, namely hydrophobic/hydrophilic, acidic/basic, or positive/negative charges.



**Fig 1.** [left] Copper(II) complexes. [middle] Photoisomerization for Arg complex. [right] Electron density around His 15.

1) H. J. Davis, T. R. Ward, *ACS Cent. Sci.*, **2019**, 5, 1120. 2) K. Kashiwagi, T. Akitsu, R. Naaman *et al.*, *Symmetry*, **2020**, 12, 808.