

Postsynthetic Asymmetric Transformation of Boronic-Acid-Protected Gold Nanoclusters Studied by Magnetic Circular Dichroism (MCD) and Electronic Circular Dichroism (ECD)

Hiroshi Yao, Masanori Saeki

Graduate School of Material Science, University of Hyogo, Hyogo 678-1297, Japan

yao@sci.u-hyogo.ac.jp

Investigations of monolayer-protected metal nanoclusters, possessing typically less than 100 atoms, are largely motivated in the past decade due to their intriguing size-dependent physicochemical properties. Much attention is recently paid on inducing chirality in metal nanoclusters owing to their widespread catalytic use of chirally-modified metal surfaces. Postsynthetic asymmetric transformation is one of the notable techniques for facile control of symmetry-breaking [1]. Our approach here is to use gold nanoclusters bearing an achiral boronic acid group that can bind to chiral *cis*-diols such as fructose [2]. In addition, we also apply magnetic circular dichroism (MCD) spectroscopy to gain a better understanding of the nanoclusters' electronic structures as well as their chiroptical signals induced by their surface fructose complexation. A relationship between the MCD and normal (induced) CD responses is also examined, both of which distinctly stem from the cluster's electronic transitions. We also find that this asymmetric induction is pH-sensitive, suggesting that the gold cluster-fructose complex formation has a great advantage for some biological applications.

We synthesized 3-mercaptophenylboronic acid (3-MPB)-protected gold clusters with a mean core diameter of 1.1 nm (gel fractioned), and examined their electronic absorption, MCD and chiroptical responses induced by the reaction of boronic acid-chiral fructose binding (Figure 1). Note that the mean core size of the cluster was determined by a solution-phase SAXS measurement. Figures 2a and 2b show absorption and MCD spectra (at a magnetic field of -1.6 T) of the gold nanocluster compound in methanol/aqueous buffer (pH = 10.0) mixture, respectively. It is well known that small gold nanoparticles ($< \sim 2$ nm) no longer support the plasmon excitation characteristic, so the structured absorption comes from molecule-like electronic transitions. On the other hand, the MCD spectrum shows overall positive features in the metal-based electronic transition region at -1.6 T. The MCD signals were very weak at $> \sim 500$ nm, probably arising from transitions out of the HOMO into LUMO (essentially intraband transitions), whereas relatively strong MCD signals were detected at higher energy transitions ($< \sim 500$ nm) that involve more or less character of thiolate ligands. Hence it is expected that the MCD responses of the thiolate-protected gold clusters would primarily arise from the electronic state mixing of the ligands and gold atoms. Note that the sign of the MCD signal was completely reversed when the field is switched ($+1.6$ T), confirming that signatures are not from an experimental artifact but originate from real MCD signals. Based on the MCD features, we deem that magnetic field-induced mixing of electronic states of the ligands and surface gold atoms would bring about the Faraday *B*-term, because (i) a ground-state Zeeman splitting (at $H = 1.6$ T) is in the order of 0.2 meV (if present), smaller than the energy of room temperature (~ 26 meV), so the *C*-term contribution should be trivial; (ii) the MCD response does not contain any derivative line shape with respect to the absorption peak, so the *A*-term contribution would be also negligible [3].

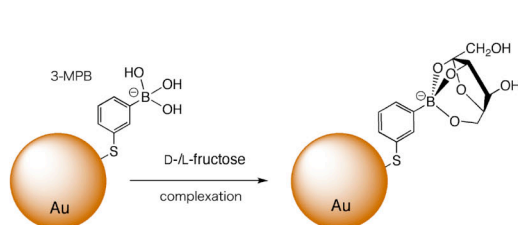


Figure 1. Reaction scheme for the postsynthetic binding between surface 3-MPB and chiral fructose bearing diols in basic solution.

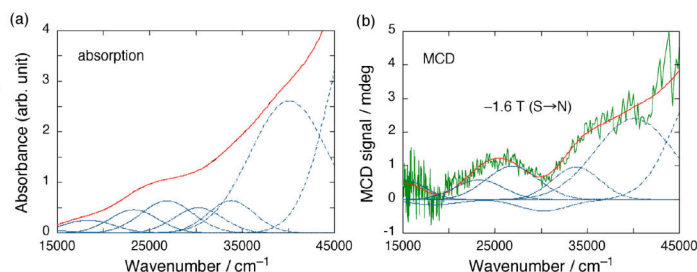


Figure 2. Absorption and MCD spectra (at -1.6 T) of the gold nanocluster compound. Deconvoluted Gaussian band fits of the electronic absorption and MCD spectra are also shown.

We next performed spectral deconvolution analysis of both the absorption and MCD data to quantitatively estimate accurate transition energies and their spectral linewidths in the nanocluster since the MCD features must correspond to electronic transitions (even unresolved) in the electronic absorption. The Gaussian fits of MCD as well as electronic absorption spectra are also shown in Figure 2. For deconvoluting the experimental data, we assumed that the analysis is constrained by the requirement that a "single set" of Gaussian components be used for the fitting of both the absorption

and the MCD spectra. For the excellent (satisfactory) agreement between the measure and calculated spectra, eight Gaussian components were necessary. Importantly, the two different spectral patterns have made the spectral deconvolution analysis successful.

The pristine gold nanocluster had no optical activity. However, D-/L-fructose addition to the nanocluster solution altered CD responses. Figure 3a shows the CD spectra of the gold nanocluster compound in the presence of D-/L-fructose at pH=10.0. Note that fructose did not induce significant absorption changes of the gold nanocluster, strongly indicating that complexation between the surface 3-MPB ligand and chiral fructose hardly influenced the electronic states of the clusters, and consequently, the gold core rearrangement or size growth was unlikely to take place upon complexation. On the other hand, the nanocluster showed an appreciable Cotton effect with complicated coupling patterns when complexed with D- or L-fructose (that is, asymmetric induction). Additionally, an almost perfect mirror-image relationship was obtained in the region of metal-based electronic transitions, implying enantiomeric complexation.

To gain a better understanding of the structure (shape) of CD spectra, we compare them with the peak-separated bands obtained by the deconvolution analysis. Figure 3b shows the induced CD and the deconvoluted absorption spectra of the gold nanocluster with D-fructose (10^{-3} M) plotted against energy in wavenumber. For the guide of eyes, vertical dash lines are drawn at the same energy positions. The induced CD response is distinctly related to the peak-separated bands; for example, the deconvoluted spectra of 2, 3, 5, 6, and 7 exhibited negative, positive, negative, positive, and negative peaks in the CD response, respectively (see Figure 3b). The band 4 showed (+/-) split-type CD signal, implying an interaction between the inclusive electronic transitions. The spectrum 1 (the lowest energy component) seems to be CD silent. In conclusion, the induced CD signatures can be successfully correlated with the isolated (separated) electronic transitions obtained by deconvolution analysis based on the absorption and MCD spectra. This spectral analysis is expected to benefit better understanding of the electronic states and the origin of the optical activity in chiral metal nanoclusters.

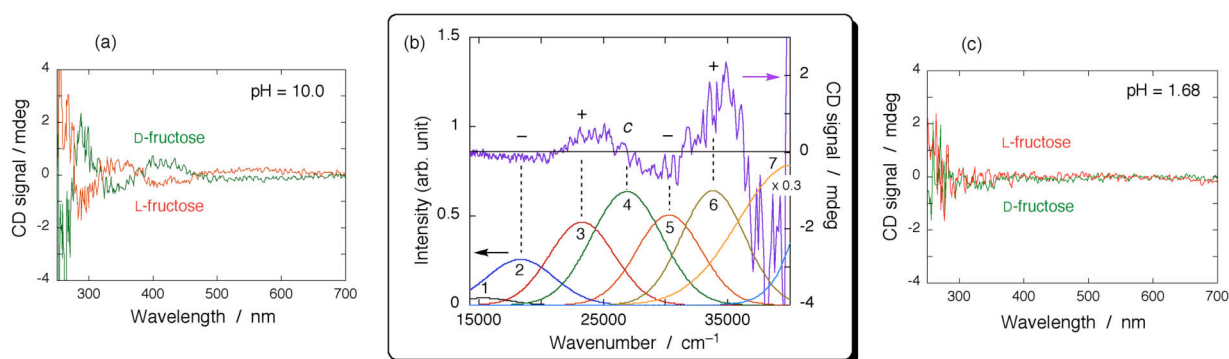


Figure 3. (a) Effects of D-/L-fructose on the CD spectrum of the 3-MPB-protected gold nanocluster in the methanolic base solution. Green and red curves indicate the spectra obtained upon addition of D- and L-fructose, respectively. Mirror image relationship can be seen between them. (b) Electronic absorption and CD spectra of the gold cluster in the presence of chiral D-fructose (10^{-3} M). The data were plotted against wavenumber. The deconvoluted spectra with Gaussian function are also shown for ease of comparison. (c) CD spectra of the gold nanocluster in the presence of D-/L-fructose (10^{-3} M) in methanolic acid solution (pH = 1.68). Green and red curves indicate the spectra obtained upon addition of D- and L-fructose, respectively.

At the end, to confirm that the induced CD responses are controllable by external parameters, we examined pH-dependent optical activity of the 3-MPB-protected gold cluster in the presence of chiral fructose. The binding constant of the anionic boronate-diol is very much larger than that of the neutral boronic acid-diol [2], so that significant decomposition of the complexes is highly expected in acidic conditions. Figure 3c shows (induced) CD spectra of the gold nanocluster compound in the presence of D-/L-fructose (10^{-3} M) in methanol/aqueous oxalate buffer (pH=1.68). In contrast to Figure 3a, no CD signals were detected, suggesting no complexation of surface 3-MPB moieties with chiral fructose. Interestingly, optical activity of the gold nanoclusters can be simply controlled by external parameters such as the pH value. This method will be a powerful strategy to quantitatively induce optical activity in a controlled manner.

References

- [1] Yao, H. Kitaoka, M.; Sasaki, A. *Nanoscale*, **4** (2012) 955.
- [2] Yao, H.; Saeki, M.; Kimura, K. *J. Phys. Chem. C*, **114** (2010) 15909.
- [3] Stephens, P. J. *Ann. Rev. Phys. Chem.*, **25** (1974) 201.