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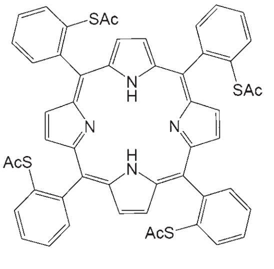
Gold(0) Porphyrins on Gold Nanoparticles**

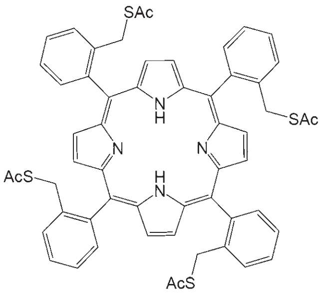
*Masayuki Kanehara, Hirokazu Takahashi, and Toshiharu Teranishi**

Gold nanoparticles play important roles in different branches of science, such as in nanoelectronics, nonlinear optics, biological labeling, and oxidation catalysis, among others.[1–5] Many ligand-functionalized metal nanoparticles have been reported based on ligation using the chemical affinity of organic functional groups toward the nanoparticle surface to stabilize the nanoparticles. Polymers,[6] linear molecules with long alkyl chains,[7] and dendrimers[8] have all been effectively used for this purpose, relying on the σ electrons of the functional groups. For the application of nanoparticles in nanoelectronic devices, exploiting the organoelectronic π-orbital interactions, which are generally used in electron-conductive polymers and organic transistors, is quite important for the reduction of the tunneling resistance of the surrounding ligands. Porphyrins are one of the most important π-conjugated compounds, and a recent study of porphyrins on Au(111)[9] encouraged us to investigate the interaction between Au nanoparticles and π-conjugated porphyrin systems. Herein, we report the preparation, structural analysis, and unique optical properties of novel porphyrin speices on Au nanoparticles. The nitrogen atoms of the porphyrin rings were found to coordinate to the Au nanoparticle surface, and the Soret-band intensity could be tuned by changing the distance between the porphyrin rings and the Au nanoparticle surface.

To obtain stable Au nanoparticles surrounded by π orbitals perpendicular to the Au surface, we focused on Au nanoparticles formed through strong multidentate ligation using thiol derivatives. As shown in Figure 1, the multidentate macrocyclic porphyrin thioester derivatives tetrakis-5,10,15,20-(2-acetylthiophenyl)porphyrin (SC_0P) and tetrakis-5,10,15,20-(2-acetylthiomethylphenyl)porphyrin (SC_1P) were synthesized. The SC_1P ligand was designed with methylene groups inserted between the benzene rings and the acetylthio groups in order to increase the distance between the porphyrin ring and the Au surface. The SC_nP ($n = 0$, 1) ligands were synthesized from the corresponding aldehyde and pyrrole using Lindsey's method[10] in 15 % and 40 % yields, respectively.[11] Since the acetylthio groups easily dissociate to form S–Au bonds on bare Au surfaces in a slightly alkaline condition,[12] these groups are considered an excellent thiol source to protect the Au surface. The SC_nP-protected Au (SC_nP-Au) nanoparticles were prepared by ligand-exchange reactions from citrate-protected Au (CA-Au) nanoparticles. After ligand exchange, the nanoparticles became insoluble in water but soluble in *N*,*N*-dimethylacetamide (DMAc), indicating that ligand exchange was accomplished. Further evidence was confirmed from X-ray photoelectron spectroscopy (XPS) measurements. The C 1s peaks assigned to the carbonyl carbon atoms of both citrate and acetylthio groups of the SC_nP ligands disappeared (Figure S1 in the Supporting Information), indicating that the citrate ligands were completely exchanged with the SC_nP ligands and that the acetylthio groups dissociated to protect the Au surface. To confirm the stability of SC_nP, these ligands were annealed with citrate and tannic acid in the absence of Au nanoparticles at 120 °C in a DMAc/water mixture. No UV/Vis spectral change was observed, thus demonstrating that the SC_nP ligands are stable under the ligand-exchange conditions.



SC_0P



SC_1P

Figure 1 shows TEM images of the CA-Au and SC_nP-Au nanoparticles. The sizes of the SC_nP-Au nanoparticles remained unchanged after the ligand exchange. The DMAc solutions of SC_nP-Au nanoparticles are quite stable under ambient conditions, and no size change was observed over at least one year because of the tetradentate nature of the SC_nP ligands. To confirm the existence of SC_nP on the Au surface and to reveal the coordination geometry, laser Raman measurements, thermogravimetric analysis (TGA), and XPS analyses were conducted. The laser Raman spectra of the SC_nP-Au nanoparticles were similar to those of the SC_nP ligands, indicating the existence of porphyrin rings on the Au nanoparticles (Figure S2 in the Supporting Information). Further evidence was obtained by cyanide decomposition of the SC_nP-Au nanoparticles.[13] When the SC_nP-Au nanoparticles were treated with an excess amount of sodium cyanide, the intensities of both the Soret band and Q band were

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[*] Dr. M. Kanehara, H. Takahashi, Prof. T. Teranishi
Graduate School of Pure and Applied Sciences
University of Tsukuba
1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81) 29-853-6503
E-mail: teranisi@chem.tsukuba.ac.jp

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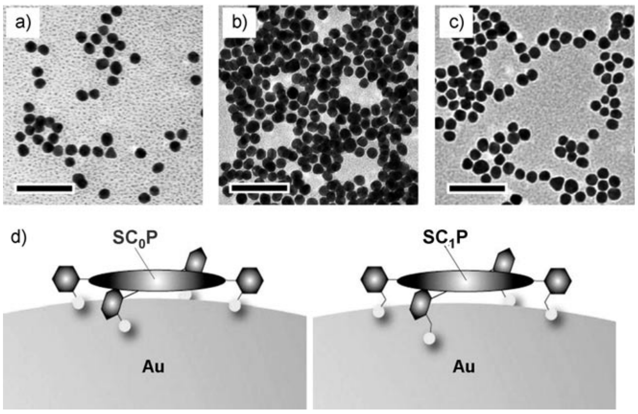

Figure 1. TEM images of a) citrate- b) SC$_0$P-, and c) SC$_1$P-protected Au nanoparticles. Particle diameters are 10.5 ± 1.0 nm (a), 10.5 ± 1.0 nm (b), and 10.0 ± 0.9 nm (c). Scale bars: 50 nm. d) Schematic illustrations of the coordination of SC$_n$P ligands on the Au surface.

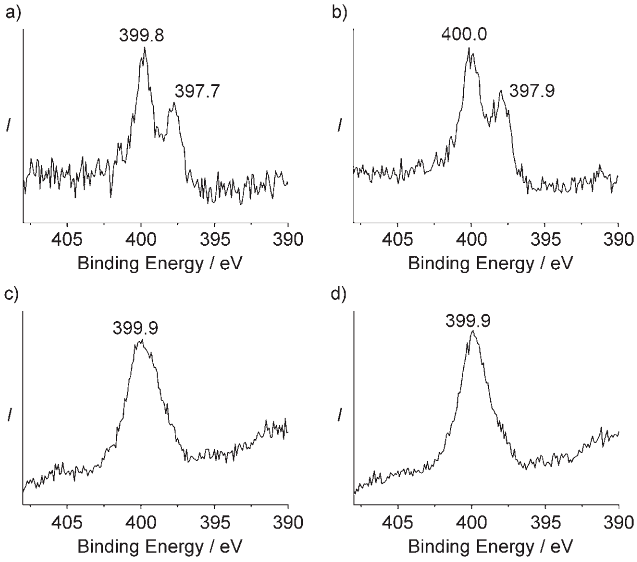

Figure 2. N 1s core-level XPS spectra for a) SC$_0$P, b) SC$_1$P, c) SC$_0$P-Au, and d) SC$_1$P-Au

recovered regardless of the decomposition of the SC$_n$P ligands (Figure S3 in the Supporting Information). TGA analysis revealed weight losses of 3.1 % and 3.0 % for SC$_0$P-Au and SC$_1$P-Au, corresponding to 246 and 226 ligands on a single Au nanoparticle for SC$_0$P-Au and SC$_1$P-Au, respectively. Considering that the length of the neighboring *meso*-substituted phenyl groups is about 1.25 nm, approximately 222 SC$_n$P ligands can cover a single Au nanoparticle surface, thus suggesting that these porphyrin ligands densely protect the Au nanoparticles in a face-coordination fashion, as shown in Figure 1 d.[11]

Further evidence for the face coordination of the SC$_n$P ligands on the Au nanoparticles could be confirmed by XPS measurements. The SC$_n$P ligands exhibit two distinct chemically inequivalent N 1s core-level spectra corresponding to free nitrogen atoms of the imine (-C=N-) and pyrrole (-NH-) groups, from lower to higher binding energy, respectively (Figure 2). However, both the SC$_0$P-Au and SC$_1$P-Au nanoparticles exhibit a single N 1s peak with a binding energy of 399.9 eV, which is similar to that of the imine nitrogen atoms coordinating to the Au(111) surface, as reported by Feringa and co-workers.[9] They observed three distinct N 1s peaks (free imine, coordinating imine, and free pyrrole) on a Au(111) substrate, whereas SC$_n$P-Au nanoparticles exhibit a single N 1s peak, indicating that the four nitrogen atoms of the SC$_n$P ligands deprotonate to coordinate to the Au surface to form Au(0) porphyrins. Although the position of the peak with a binding energy of about 399.9 eV corresponds to the binding energy of nitrogen atoms in metalloporphyrins,[9] the possibility of the formation of Au^{III} porphyrins was ruled out, because no Au 4f$_{7/2}$ peak assigned to oxidized gold was observed in SC$_n$P-Au (Figure S4 in the Supporting Information). We conclude that this unique coordination fashion is a nanoparticle effect. The porphyrin derivatives are expected to coordinate mainly to the step edges and plane boundaries that the nanoparticles possess on their surfaces, centering at the porphyrin nitrogen atoms. To the best of our knowledge, this coordination fashion resulting from the porphyrin molecules spontaneously deprotonating to coordinate to a zero-valent metal surface has never been reported, not only for porphyrins on bulk Au(111) or Ag(111) surfaces but also for previously reported Ru^0 and Fe^0 porphyrins. Furthermore, the Ru^0[14] and Fe^0[15] porphyrins have a quite high reactivity toward both organic and inorganic electrophiles, while our SC$_n$P-Au nanoparticles are exceedingly stable against various electrophiles including water and DMAc, and no decomposition of the SC$_n$P ligands on the Au nanoparticles was observed by UV/Vis spectra under ambient conditions. The ligand-exchange conditions were almost pH-neutral, and UV/Vis spectral changes are not observed for the SC$_n$P-Au nanoparticles after adding acetic acid to the SC$_n$P-Au nanoparticle solution. Thus, it was concluded that the deprotonation of the porphyrins was not induced by some bases. Presumably, the strong tetradentate coordination of the SC$_n$P ligands fixes the porphyrin rings onto the Au nanoparticle surfaces to stabilize the deprotonated porphyrin rings. In addition, refluxing a toluene solution containing Au nanoparticles, tetraphenylporphyrin, and dodecanethiol did not result in Au^0 porphyrin formation.

Interestingly, these SC$_n$P-Au nanoparticles exhibit unique optical properties. Figure 3 shows the UV/Vis spectra of the DMAc solutions containing SC$_n$P ligands or SC$_n$P-Au nanoparticles. The DMAc solutions of SC$_0$P and SC$_1$P gave Soret bands at 421 and 423 nm, respectively, and four distinct Q bands in the range 515–646 nm. Upon coordination of the SC$_n$P ligands onto the Au nanoparticles, the Q bands for the SC$_n$P-Au nanoparticles completely disappeared, and the Soret bands for the SC$_0$P-Au and SC$_1$P-Au nanoparticles were broadened and red-shifted to 432 and 427 nm, respectively. The molar absorption coefficients of the Soret bands for the SC$_0$P-Au and SC$_1$P-Au nanoparticles were calculated to be 2.5×10^4 and $7.0 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$, respectively, using TGA results and subtraction of the Au nanoparticle background. These values are smaller by one order of magnitude than those for the SC$_n$P ligands themselves (ca. $3.9 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$).

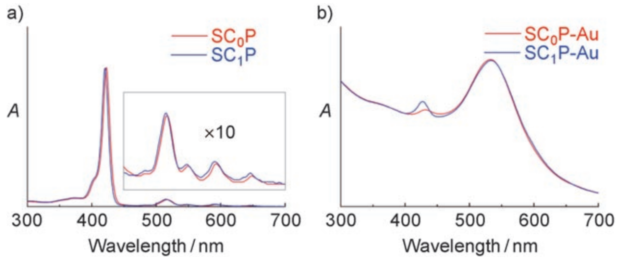

Figure 3. UV/Vis spectra of a) SC$_n$P ligands and b) SC$_n$P-Au nanoparticles. The inset in (a) shows the Q bands expanded by 10. Each set of spectra was normalized by ligand (a) and nanoparticle (b) concentrations.

These results are completely different from those of the Au nanoparticles protected by *meso*-3-acetylthiophenyl-substituted porphyrin[16] and other porphyrin derivatives,[17,18] in which the porphyrin rings are tilted at the Au surface and the extensive diminishing of both the Soret band and Q band has not been observed. The drastic changes in the absorbance of the Soret band and Q band for porphyrin molecules on Au nanoparticles have to result from the change in electronic state of the porphyrins. Generally, a red-shift of the Soret band results from the formation of a side-by-side partially π–π stacked structure of the J aggregate type,[19] although the formation of J aggregates cannot explain the decrease in intensity of the Soret band and Q band of the SC$_n$P-Au nanoparticles. Distortion of the porphyrin ring may lead to a decrease in the Soret-band intensity, although a large distortion of the porphyrin ring must accompany the considerable shift of the Soret band.[20] Thus, this distortion model is not applicable to our case, because red-shifts of only a few nanometers are observed for the SC$_n$P-Au nanoparticles. Though the details are not understood yet, the unique optical change exhibited by the porphyrin rings may be derived from the direct interaction between the porphyrin π and Au orbitals, in other words, from the partial charge transfer between the porphyrin and Au surface, which is often observed between porphyrin rings and fullerenes.[21] Another possibility includes the hybridization of the porphyrin π and Au orbitals to form new orbitals between the porphyrin rings and Au surfaces, as calculated for a conductive carbon nanotube on an aluminum surface.[22] Considering the longer porphyrin–Au distance for SC$_1$P-Au, as illustrated in Figure 1 d, the Au–porphyrin interaction for SC$_0$P-Au is expected to be much larger than that for SC$_1$P-Au, resulting in the larger red-shift and the broadening of the Soret band for SC$_0$P-Au.

In conclusion, we have synthesized macrocyclic porphyrin ligands which protect Au nanoparticles with the porphyrin rings parallel to the Au surface. The porphyrin rings on the Au nanoparticles have a stronger coordination ability to the Au surface than to a Au(111) substrate, since all imine nitrogen atoms of the SC$_n$P ligands participate in the ligation to the Au nanoparticle surface to form quite stable Au^0 porphyrins. The Au^0 porphyrin has a novel structure in that the porphyrin molecule on the Au nanoparticle surface has been deprotonated to coordinate to a surface Au atom, and such a coordination fashion is completely different from that displayed by conventional metalloporphyrins, in which the porphyrin coordinates to an isolated metal ion. The SC$_n$P-Au nanoparticles show a ligand-dependent decrease of the Soret-band intensity, whereby the shift and decrease of the Soret band for SC$_0$P-Au are larger than those for SC$_1$P-Au. The diminishing of the Soret band, which is tuned by the coordination distance between the porphyrin ring and the Au surface, implies an electronic interaction between the porphyrin and Au nanoparticle. A first-principles calculation approach to confirm our claim is currently in progress.

Experimental Section

Preparation of SC$_n$P-Au nanoparticles: Citrate-capped Au (CA-Au) nanoparticles with a size of 10.5 ± 1.0 nm were prepared according to the literature.[23] The CA-Au aqueous solution was poured into the same volume of a *N,N*-dimethylacetamide (DMAc) solution of SC$_n$P, where a half equivalent of ligand to surface Au atoms was used based on the spherical model.[24] Because the SC$_n$P ligands have four atropisomers at room temperature,[25] the DMAc solution of the nanoparticles was annealed at 120 °C to promote the coordination of four thiolate groups onto the same nanoparticle surface. After removing the solvent under reduced pressure, water was added and the resulting precipitate was filtered and washed with water, methanol, and toluene to obtain pure SC$_n$P-Au nanoparticles. Purification was checked by analytical gel permeation chromatography.

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