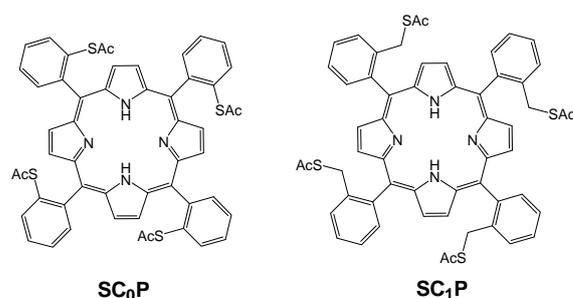# Gold(0) Porphyrins on Gold Nanoparticles [**]

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Gold (Au) nanoparticles play important roles in different branches of science, such as in nanoelectronics, nonlinear optics, biological labeling, oxidation catalysis, etc.[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 in order 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 etc., are quite important in light of the reduction of the tunneling resistance of the surrounding ligands. Porphyrin is one of the most important π-conjugated compound and recent study of porphyrin on Au(111)[9] encouraged us to investigate the interaction between Au nanoparticle and porphyrin π-conjugated system. In this communication, we report the preparation, structural analysis and unique optical properties of novel porphyrin speices on Au nanoparticles. The nitrogen atoms of porphyrin rings were found to have coordination ability 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, multidentate macrocyclic porphyrin-thioester derivatives, tetrakis-5,10,15,20-(2-acetylthio-phenyl)porphyrin (SC_0P) and tetrakis-5,10,15,20-(2-acetylthio-methylphenyl) 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 sulfur-Au bonds on

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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 XPS measurements, that is, the C1s peaks assigned to the carbonyl carbon of both citrate and acetylthio groups of SC_nP ligands disappeared (Figure S1), indicating that the citrate ligands were completely exchanged with the SC_nP ligands and that the acetylthio groups dissociated to protect Au surface. In order 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 DMAc/water mixed solvent. No UV-Vis spectral change was observed, demonstrating that the SC_nP ligands are stable in the ligand-exchange condition.

Figure 1 shows the TEM images of 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 has been observed at least within one year due to the tetradentate nature of the SC_nP ligands. In order to confirm the existence of SC_nP on the Au surface and reveal the coordination geometry, Laser Raman measurements, thermogravimetric analysis (TGA) and XPS analysis 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). Further evidence was obtained by cyanide decomposition of SC_nP-Au nanoparticles.[13] When the SC_nP-Au nanoparticles were treated with an excess amount of sodium cyanide,
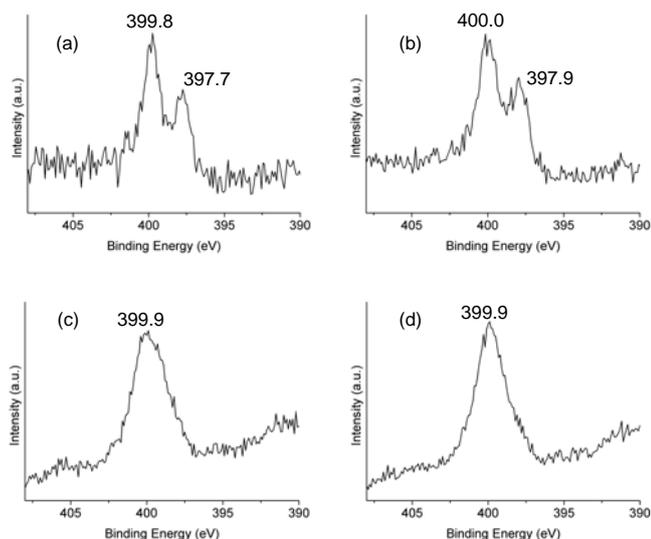

SC₀P   **SC₁P**
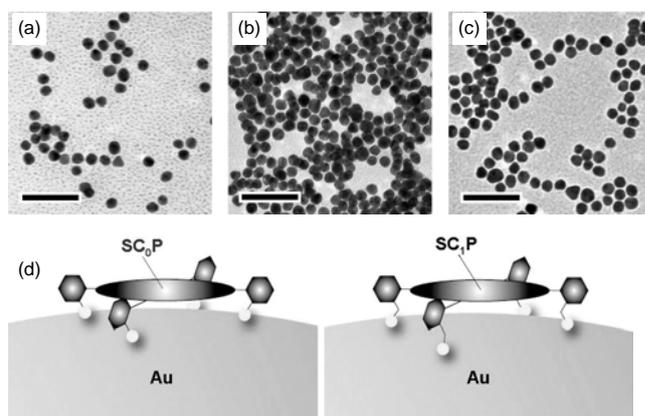
Figure 1. TEM images of (a) citrate- (b) SC_0P- and (c) SC_1P-protected Au nanoparticles. Particle diameters are (a) 10.5 ± 1.0 nm, (b) 10.5 ± 1.0 nm and (c) 10.0 ± 0.9 nm, respectively. Scale bar indicates 50 nm. (d) Schematic illustrations of the coordination of SC_nP ligands on the Au surface.

Figure 2. N1s core level XPS spectra for (a) SC_0P, (b) SC_1P, (c) SC_0P-Au and (d) SC_1P-Au

Figure 3. UV-Vis spectra of (a) SC_nP ligands and (b) SC_nP-Au nanoparticles. Inset in (a) shows the Q-bands expanded by 10. Each set of spectra was normalized by (a) ligand and (b) nanoparticle concentrations.

the intensities of both the Soret-band and Q-band were recovered regardless of the decomposition of the SC_nP ligands (Figure S3). TGA analysis revealed the weight losses of 3.1 % and 3.0 % for SC_0P-Au and SC_1P-Au, corresponding to the number of ligands on a single Au nanoparticle to be 246 and 226 for SC_0P-Au and SC_1P-Au, respectively. Considering the length of the neighbouring meso-substituted phenyl groups are about 1.25 nm, 222 SC_nP ligands can cover a single Au nanoparticle surface, suggesting that these porphyrin ligands densely protect the Au nanoparticles in a face-coordination fashion, as shown in Figure 1d.[11]

Further evidence for the face coordination of SC_nP ligands on Au nanoparticles could be confirmed by XPS measurements. The SC_nP ligands exhibit two distinct chemically-inequivalent N1s core-level spectra corresponding to free iminic (-C=N-) and pyrrolic (-NH-) nitrogens, from lower to higher binding energy, respectively (Figure 2). On the other hand, both SC_nP-Au nanoparticles exhibit a single N1s peak with a binding energy at 399.9 eV, which is similar to that of the iminic nitrogens coordinating to the Au(111) surface, as reported by Feringa and co-workers.[9] They observed three distinct N1s peaks (free iminic, coordinating iminic and free pyrrolic) on Au(111) substrate, whereas SC_nP-Au nanoparticles exhibit a single N1s peak, indicating that the four nitrogen atoms of the SC_nP ligands dehydrate to coordinate to the Au surface to form Au(0) porphyrins. Although the position of the peak with a binding energy at ca. 399.9 eV corresponds to the binding energy of nitrogen atoms in metalloporphyrins,[9] the possibility of the formation of Au(III)porphyrin was denied, because no Au $4f_{7/2}$ peak assigned to oxidized gold was observed in SC_nP-Au (Figure S4). We conclude this unique coordination fashion as 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 nitrogens. To the best of our knowledge, this coordination fashion that the porphyrin molecules were spontaneously dehydrated to coordinate on zero valent metal 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 quite high reactivity with both organic and inorganic electrophile, while our SC_nP-Au nanoparticles are extensively stable against various electrophile including water and DMAc, and no
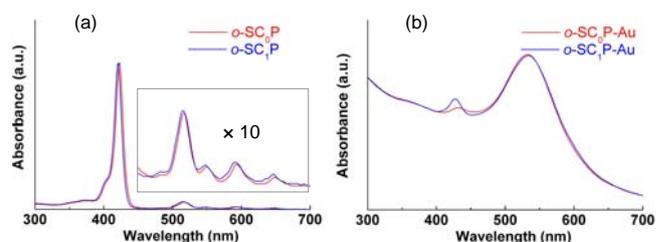
decomposition of SC_nP ligands on Au nanoparticles was observed by UV-Vis spectra under ambient condition. The ligand exchange condition was almost neutral and the UV-vis spectral changes are not observed for the SC_nP-Au nanoparticles after adding acetic acid to the SC_nP-Au nanoparticles solution. Thus, it was concluded that the deprotonation of the porphyrins was not induced by some bases. Presumably, the strong tetradentate coordination structure of SC_nP ligands fixes the porphyrin rings on Au nanoparticle surfaces to stabilize the deprotonated porphyrin rings. In addition, refluxing the toluene solution containing Au nanoparticles, tetraphenylporphyrin, and dodecanethiol did not result in the Au(0) porphyrin formation.

Interestingly, these SC_nP-Au nanoparticles exhibited unique optical properties. Figure 3 shows the UV-Vis spectra of the DMAc solutions containing SC_nP ligands or SC_nP-Au nanoparticles. The DMAc solutions of SC_0P and SC_1P gave Soret-bands at 421 and 423 nm, respectively, and four distinct Q-bands in the range from 515 nm to 646 nm. On coordinating SC_nP ligands on Au nanoparticles, the Q-bands for SC_nP-Au nanoparticles completely disappeared and the Soret-bands for the SC_0P-Au and SC_1P-Au nanoparticles were broadened and red-shifted to 432 and 427 nm, respectively. The molar absorption coefficients of the Soret-bands for the SC_0P-Au and SC_1P-Au nanoparticles were calculated to be 2.5×10^4 and 7.0×10^4 $M^{-1}cm^{-1}$, respectively, using TGA results and subtraction of the Au nanoparticle background. These values are smaller by one order of magnitude than those for SC_nP ligands themselves, ~3.9×10^5 $M^{-1}cm^{-1}$.

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] where the porphyrin rings are tilting at the Au surface and the extensive diminishing of both the Soret-band and Q-band were not observed. The drastic change in the absorbance of Soret-band and Q-band for porphyrin molecules on Au nanoparticles have to result from the change in electronic state of porphyrins. Generally, a red-shift of the Soret band results from the formation of a side-by-side partially π-π stacked J-aggregate-like structure,[19] although the formation of J-aggregates cannot explain the decrease in intensity of the Soret-band and Q-band of the SC_nP-Au nanoparticles. Distortion of the porphyrin ring may lead to the 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 only a few nanometer red-shifts are observed for the SC_nP-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, the partial charge transfer between the porphyrin and Au, which is often observed between the 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 the conductive carbon nanotube on aluminum surface.[22] Considering the longer porphyrin-Au distance for SC_1P-Au, as illustrated in Figure 1d, the Au-porphyrin interaction for SC_0P-Au is expected to be much larger than that for SC_1P-Au, resulting in the larger red-shift and the broadening of the Soret band for SC_0P-Au.

In conclusion, we have synthesized macrocyclic porphyrin ligands (SC_0P and SC_1P) which protect Au nanoparticles with the porphyrin rings parallel to the Au surface. The porphyrin rings on Au nanoparticles have stronger coordination ability to Au surface than that to Au(111) substrate, since all iminic nitrogen atoms of SC_nP ligands participate the ligation to the Au nanoparticle surface to form quite stable Au(0) porphyrins. The Au(0) porphyrin has a novel structure that the porphyrin molecule on the Au nanoparticle surface was dehydrated to coordinate to the surface Au atom and such coordination fashion is completely different from the conventional metalloporphyrins, which coordinate to the isolated metal ions. The SC_nP-Au nanoparticles show a ligand-dependent decrease of the Soret-band intensity, where the shift and decrease of the Soret-band for SC_0P-Au are larger than those for SC_1P-Au. The extinction 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 principle calculation approach to confirm our claim is currently in progress.

Experimental Section

Preparation of SC_nP-Au nanoparticles.

Citrate-capped Au (CA-Au) nanoparticles with the 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 the SC_nP *N,N*-dimethylacetamide (DMAc) solution, where 1/2 equivalent of ligand to surface Au atoms was used based on the spherical model.[24] Because the SC_nP 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_nP-Au nanoparticles. Purification was checked by analytical gel permeation chromatography.

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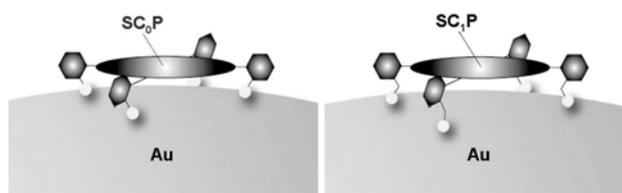
Multidentate macrocyclic porphyrin-thioester derivatives densely protect the Au nanoparticles in a face-coordination fashion to form quite stable Au(0) porphyrins. The decrease in the Soret-band intensity can be tuned by the distance between the porphyrin ring and the Au surface.