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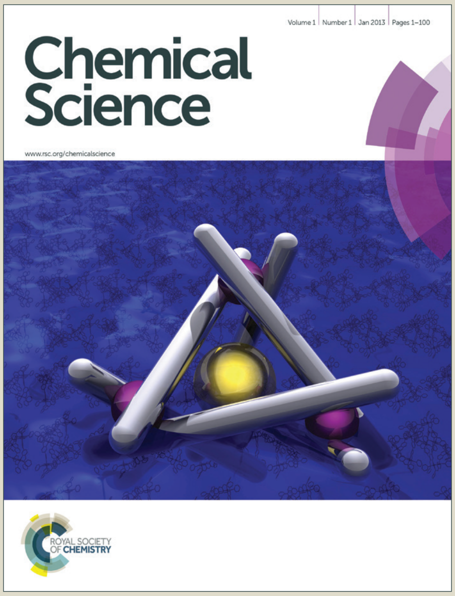

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Strongest π-Metal Orbital Coupling in a Porphyrin/Gold Cluster System†

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Abstract Face-on and close configuration of π-conjugated molecule on Au cluster generate the strong π-metal coupling between π orbital and metal orbital. We successfully synthesized porphyrin-coordinated Au clusters in face-on configuration at the closest distance. The interaction between Au cluster and porphyrin was investigated by UV-vis-NIR and transient absorption measurement.

The configuration of a π-conjugated molecule on a metal surface is an important factor in determining the molecule-metal interfacial interaction because the interfacial interaction is affected by π-metal coupling. Because π-metal coupling significantly improves electron transport through molecule-metal junctions, the control of molecular configuration is important for the development of nanoelectronic and photoenergy conversion devices.[1-7] A face-on and close configuration of a molecule on a metal surface generates the strongest coupling between the π orbitals of molecules and metal orbitals, and this causes a broadening and shifting of the energy levels of the π-conjugated molecule and modifies molecular conductance.[3,8-12] Heimel et al. demonstrated that the electronic structure of pentacene derivatives dramatically changed when their π orbitals closely approached a metal surface in a face-on configuration.[6] Tao et al. demonstrated that π-metal coupling greatly modified the conductance of a single ladder-type pentaphenylene bridged between an Au(111) electrode and an Au STM tip.[4]

The introduction of π-metal coupling to the interface between molecules and an Au cluster (AuC) is expected to modify the performance of various devices containing the clusters. Electron transport between AuCs and electrodes is important in the development of photoenergy conversion[7] and nanoelectronic devices.[13] π-Metal coupling results in highly efficient electron transport because of (i) a modulation of the energy levels of molecules on AuCs and/or (ii) a thinning of the organic ligand layer.[1,4-6,14] Furthermore, any change in the electronic structure of a π-conjugated molecule should modulate the photoinduction behavior of composites.[2,7] However, the properties of π-conjugated molecule-coordinated AuCs with a strong π-metal coupling have not been well studied owing to the difficulty of synthesis of such AuCs. In addition, the theoretical prediction of π-metal coupling for a huge π-conjugated molecule/AuC system is extremely difficult because of computational constraints. Currently, experimental investigation is the most effective method to study π-metal coupling.

We have previously synthesized porphyrin-cooridnated Au nanoparticles (~10 nm) in a face-on configuration.[15] In general, the electronic structure of Au nanostructures dramatically change depending of their sizes. The nanoparticles (> 2 nm) exhibit the metal-like properties while the AuCs (< 2 nm) exhibit molecular-like properties due to the discrete electronic structure.[16] Therefore, the systematic study for strong π-metal coupling between the porphyrin and the quantized AuC is an important subject in light of not only scientific interests but also their applications, such as single electron transistor (SET).[13,17] We also reported the synthesis of porphyrin-coordinated AuCs in a face-on configuration,[14] in which the porphyrin ring settled ~3.4 Å above the AuC. Herein, we report the strongest π-metal coupling system to date upon the synthesis of novel porphyrin-coordinated AuCs (1.9 nm) with the closest distance known between a porphyrin ring and a AuC surface (~2.6 Å). The structure of the porphyrin-coordinated AuC was characterized by atomic resolution high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The interaction between the porphyrin and the AuCs was investigated by UV-vis-NIR and transient absorption (TA) measurements.

For this closest approach between a porphyrin and an AuC we synthesized tetrakis-5*α*,10*α*,15*α*,20*α*-(2-acetylthiophenyl)porphyrin (SC_0P) (Figure 1a).[15] SC_0P contains four acetylthio groups (i.e., binding sites to the AuC) facing the same direction toward the porphyrin ring. This led to a face-on configuration for the porphyrin on the AuCs through quadridentate coordination (Figure 1c). To investigate the distance-dependent interaction between the porphyrin and the AuCs we also synthesized tetrakis-5*α*,10*α*,15*α*,20*α*-(2-acetylthiomethylphenyl)porphyrin (SC_1P) and tetrakis-5*α*,10*α*,15*α*,20*α*-(2-acetylthioethylphenyl)porphyrin (SC_2P) (Figure 1a).[14,15] The SC_0P binding sites are directly connected to the *meso*-substituted phenyl groups while SC_1P and SC_2P contain methylene spacers (i.e., distances between the porphyrin ring and the sulfur atoms were ~2.6, ~3.4, and 4.85 Å for SC_0P, SC_1P, and SC_2P, respectively) (Figure 1b).[14,18] The SC_nP (n = 0 ~ 2)-coordinated AuCs (SC_nP□AuCs) were synthesized by the reduction of Au^{III} ions with excess $NaBH_4$ at 200 K in the presence of SC_nP. The obtained SC_nP□AuCs were purified by gel permeation chromatography

(GPC) to remove free SC$_n$P and to remove byproducts. SC$_1$P–AuC and SC$_2$P–AuC were hexahedron-shaped nanomaterials composed of six porphyrin derivatives and a spherical AuC of ~1 nm in size. Their chemical compositions were Au$_{\sim65}$(SC$_1$P)$_{\sim6}$ and Au$_{\sim66}$(SC$_2$P)$_{\sim6}$.[14] Figures 2a and b show a TEM image of SC$_0$P–AuCs and the size distributions of the SC$_n$P–AuCs. The sizes of the AuCs were 1.9 ± 0.3, 1.2 ± 0.2, and 1.1 ± 0.1 nm for SC$_0$P–, SC$_1$P–, and SC$_2$P–AuCs, respectively.[14] The size of the SC$_0$P–AuCs is larger than that of the SC$_1$P– or SC$_2$P–AuCs. From the GPC chromatogram, the SC$_0$P–AuCs showed a peak at 17.0 min, which is 1.3 min faster than the peaks of SC$_1$P– and SC$_2$P–AuCs (18.3 min), indicating that the volume of SC$_0$P–AuC is larger than that of SC$_1$P– or SC$_2$P–AuC (see Figure S1 in SI). Furthermore, the peak shapes of the SC$_n$P–AuCs showed a Gaussian distribution indicating that the SC$_n$P–AuCs are highly monodispersed. These GPC results agreed well with the TEM observation. The larger SC$_0$P–AuCs can be explained by the rigidity of the SC$_0$P framework. Recently, we reported that the length of the binding sites of rigid bidentate ligands determines the size of the generated Au nanoparticles (AuNPs).[19] Because the sulfur atoms of SC$_0$P are rigid compared with SC$_1$P and SC$_2$P, a similar size-focusing effect was thought to be at work in the present case.

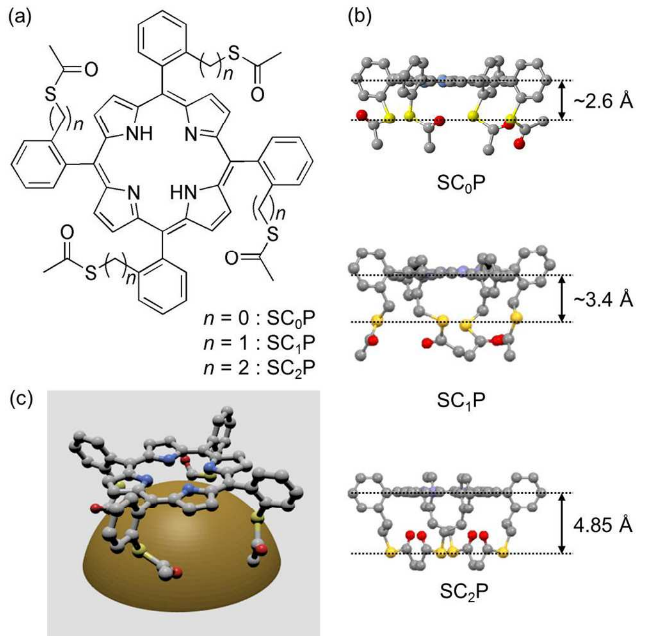

Figure 1. (a) Chemical structure and (b) side views of the steric structure for SC$_n$P (n = 0 ~ 2). (c) Schematic illustration of the face-on configuration of SC$_0$P on an AuC surface.

The Au core structure of a SC$_0$P–AuC was investigated by HAADF-STEM and by simulation using CrystalMaker (ver. 2.3.5). In the HAADF-STEM images of the SC$_0$P–AuC in the <110> zone axis, single crystal or twinned face-centered-cubic (fcc) AuCs were observed (Figure 2c). Twinned AuCs are attributed to the formation of small twinned Au cores after the reduction of Au^{III} ions and subsequent epitaxial growth. The surface of the AuC was enclosed by both {111} and {100} facets, and the twin boundary of the twinned AuC was a {111} plane, which is a representative slip plane in the fcc lattice. Structural models of the single crystalline cuboctahedral AuC and the twinned AuC were obtained by removing the Au atoms from a bulk fcc Au crystal to form AuCs with the experimentally observed size, shape, and surface. From the structural model, the number of Au atoms in an AuC was estimated to be 309.

The number of SC$_0$P on an AuC was determined by ICP-AES. The Au to S amount-of-substance ratio was found to be 85:15, indicating that 14 SC$_0$P molecules attached to a single AuC. UV-vis-NIR absorption spectrum of SC$_0$P–AuCs indicates a face-on configuration for porphyrins on the AuCs (vide infra). The surface area of an AuC corresponds to that of 14 porphyrin rings. Furthermore, a GPC chromatogram of the SC$_0$P–AuCs indicates that the SC$_0$P–AuCs were highly monodispersed. Consequently, we propose that a major component of SC$_0$P–AuC is a 14 porphyrin-coordinated Au$_{309}$ cluster in a face-on configuration as shown in Figure 2d.

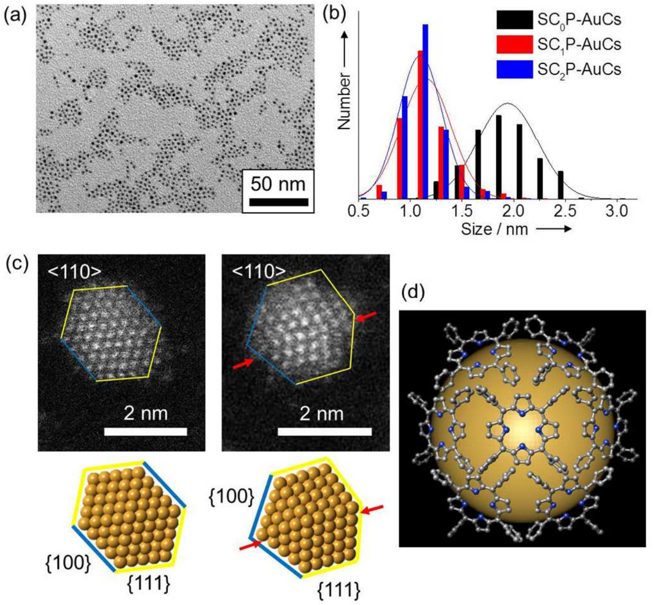

Figure 2. (a) TEM image of SC$_0$P–AuCs. (b) Size distributions of the SC$_n$P–AuCs. The sizes of the AuCs in SC$_0$P–, SC$_1$P–, and SC$_2$P–AuCs are 1.9 ± 0.3, 1.2 ± 0.2, and 1.1 ± 0.1 nm, respectively. (c) HAADF-STEM images and structural models of the single crystal structure (left) and the twinned structure (right). Arrows represent the twin boundary in an AuC. (d) Proposed structure of SC$_0$P–AuC.

We also investigated how the large π-metal coupling affects the electronic state of SC$_n$P on an AuC. Figure 3a and b shows the absorption spectra of free SC$_n$P and SC$_n$P–AuCs. The absorption spectra of the SC$_n$P–AuCs showed a decreasing abosorbance from the visible to the NIR region and this is assigned to inter- and intraband absorption of the AuCs. For SC$_0$P–AuCs, a localized surface plasmon band from 500 to 600 nm was observed owing to their larger diameter. Free SC$_n$P exhibited Soret bands (S$_0$ → S$_2$ transition) at ~420 nm and four distinct Q bands (S$_0$ → S$_1$ transition) from 512 to 664 nm. On the contrary, the Soret bands of SC$_n$P on the

AuCs were dramatically broader and red-shifted, depending on the distance between the porphyrin rings and the AuCs. These spectral changes are typical for the face-on configuration of porphyrins on AuCs.[14,15] The molar absorption coefficients of the Soret bands decreased up to 8% (from 3.8×10^5 to 3.2×10^4 $M^{-1}cm^{-1}$), 9% (from 3.9×10^5 to 3.5×10^4 $M^{-1}cm^{-1}$), and 38 % (from 3.9×10^5 to 1.5×10^5 $M^{-1}cm^{-1}$) for SC_0P–, SC_1P–, and SC_2P–AuCs, respectively. The peak positions of the Soret bands were red-shifted by 18 and 5 nm for SC_0P–, and SC_1P–AuCs, respectively, while no red-shift was observed for the Soret band of SC_2P on AuCs. The spectral change of SC_0P on the AuCs was dramatic compared with SC_1P and SC_2P on the AuCs. It is known that the face-on approach of π-conjugated molecules to an Au surface causes a shift in the energy levels of a π-conjugated molecule on an Au surface because of the image-charge effect,[3,6,8] and a closer approach induces a broadening of the energy levels because of π-metal coupling.[3,6,8-12] The above spectral changes can likely be attributed to the image-charge effect and π-metal coupling.[20] In addition, the spectral change of the SC_0P on the AuC resembles that of the SC_0P on the plasmonic Au nanoparticle (~10 nm),[15] suggesting that the localized surface plasmon resonance and the electronic structure of Au core might not significantly influence the π-metal coupling.

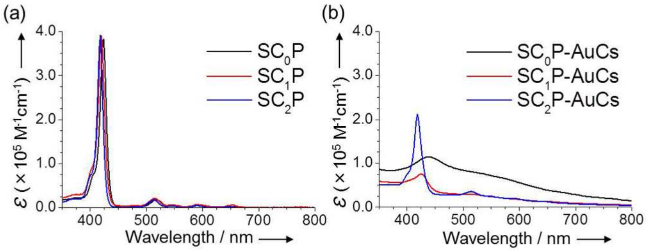

Figure 3. UV-vis-NIR absorption spectra of a) free SC_nP and b) SC_nP□AuCs in DMF.

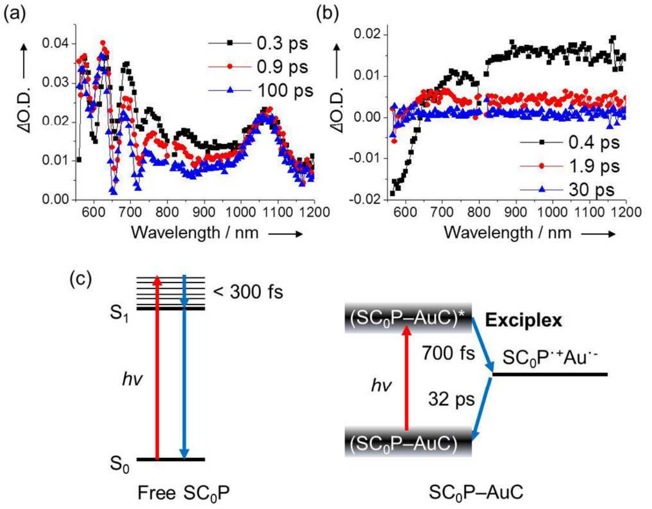

Figure 4. TA spectra of a) free SC_0P and b) SC_0P□AuCs in DMF after excitation using a 520-nm laser. (c) Energy diagrams of free SC_0P and SC_0P□AuC.

The excited state behavior of the SC_0P–AuCs was investigated by TA measurements because it provides important information about changes in density of state and molecule-metal interactions. Figure 4a and b shows the TA spectra of free SC_0P and SC_0P–AuCs in DMF after excitation at 520 nm. Upon the excitation of free SC_0P, a bleaching of the Q bands and a characteristic peak at ~1070 nm, which is assigned to the S_1 state of the porphyrin were observed (Figure 4a,c). The decreasing absorbance from 500 to 1000 nm quickly sharpened because of vibrational relaxation. Conversely, SC_0P–AuCs exhibited a broad absorption from 650 to 1200 nm and a bleaching of the Q band from 550 to 650 nm at 0.4 ps after excitation (Figure 4b). Because a broad absorption was observed with the bleaching of the Q band of the porphyrin, this cannot be attributed to the AuC cores. Additionally, the spectral shape differs from that of the S_1 state or the radical cation of porphyrin.[22,23] Thus, we suggest that the broad absorption should be caused by the enhanced π-metal coupling in the excited state and assigned to an "exciplex".[20] At 1.9 ps after excitation, a broad peak at ~680 nm, assigned to the radical cation, was observed.[22,23] From the above results, the photoinduced behavior of SC_0P–AuCs can be described as follows. Immediately after excitation, the SC_0P–AuCs form an exciplex. An ultrafast charge separation proceeds from the exciplex (700 fs) and a recombination to the ground state (32 ps) occurs (Figure 4c, see Figure S2 in SI for the decay profile). Similar photoinduced behavior was reported for a porphyrin/fullerene system in a face-on configuration.[22] TA spectra of SC_1P–, and SC_2P–AuCs have not been obtained because of the current low stability of clusters when using lasers.[24]

Conclusions

In this study, we successfully synthesized SC_0P–AuCs and investigated the interfacial interaction between the porphyrin and AuCs. Spectroscopic investigations indicate that a strong π-metal coupling exists between the porphyrin and the AuCs in the ground state, which results in the formation of an exciplex upon photoexcitation. This is the first observation of an exciplex between π-conjugated molecules and a pure metal. The SC_0P–AuCs are promising as Coulomb islands in SET because the tunneling resistance between these Coulomb islands and the source/drain electrodes will decrease significantly. The development of low voltage- and room temperature-driven SETs is in progress.

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† Electronic Supplementary Information (ESI) available: Synthesis of SC$_n$P and SC$_n$P□AuCs. Computational method. GPC chromatogram of SC$_n$P□AuCs. Decay profile for free SC$_0$P and SC$_0$P–AuCs. See DOI: 10.1039/c000000x/

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