Strongest \( \pi \)--metal orbital coupling in a porphyrin/gold cluster system†

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Face-on and close configuration of a \( \pi \)--conjugated molecule on an Au cluster generates a strong \( \pi \)--metal coupling between the \( \pi \) and metal orbitals. We successfully synthesized porphyrin-coordinated Au clusters in face-on configuration at the closest distance. The interaction between the Au cluster and porphyrin was investigated by UV-vis-NIR and transient absorption measurement.

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

The introduction of \( \pi \)--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\textsuperscript{7} and nanoelectronic devices.\textsuperscript{13} \( \pi \)--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.\textsuperscript{1,4–6,14} Furthermore, any change in the electronic structure of a \( \pi \)--conjugated molecule should modulate the photoinduction behavior of the composites.\textsuperscript{2,7} However, the properties of \( \pi \)--conjugated molecule-coordinated AuCs with a strong \( \pi \)--metal coupling have not been well studied owing to the difficulty of synthesis of such AuCs. In addition, the theoretical prediction of \( \pi \)--metal coupling for a huge \( \pi \)--conjugated molecule/AuC system is extremely difficult because of computational constraints. Currently, experimental investigation is the most effective method to study \( \pi \)--metal coupling.

We have previously synthesized porphyrin-coordinated Au nanoparticles (~10 nm) in a face-on configuration.\textsuperscript{15} In general, the electronic structure of Au nanostructures dramatically change depending on their sizes. Nanoparticles (>2 nm) exhibit metal-like properties while the AuCs (<2 nm) exhibit molecular-like properties due to their discrete electronic structure.\textsuperscript{16} Therefore, the systematic study for strong \( \pi \)--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 for single electron transistors (SETs).\textsuperscript{13,17} We also reported the synthesis of porphyrin-coordinated AuCs in a face-on configuration,\textsuperscript{14} in which the porphyrin ring settled ~3.4 Å above the AuC. Herein, we report the strongest \( \pi \)--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-5₂,10₂,15₂,20₂-(2-acetylthiophenyl)porphyrin (SC₀P) [Fig. 1a].¹⁴ SC₀P contains four acetythio 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 (Fig. 1c). To investigate the distance-dependent interaction between the porphyrin and the AuCs we also synthesized tetrakis-5₂,10₂,15₂,20₂-(2-acetylthioethylphenyl)porphyrin (SC₁P) and tetrakis-5₂,10₂,15₂,20₂-(2-acetyltioethylphenyl)porphyrin (SC₂P) [Fig. 1a].¹⁴,¹⁵ The SCₙP binding sites are directly connected to the meso-substituted phenyl groups while SC₁P and SC₂P contain methylene spacers (i.e., distances between the porphyrin ring and the sulfur atoms were ~2.6, ~3.4 and 4.85 Å for SC₀P, SC₁P and SC₂P, respectively) (Fig. 1b).¹⁴,¹⁵ The SCₙP (n = 0–2)-coordinated AuCs (SCₙP–AuCs) were synthesized by the reduction of Au¹⁺ ions with an excess of NaBH₄ at 200 K in the presence of SCₙP. The obtained SCₙP–AuCs were purified by gel permeation chromatography (GPC) to remove free SCₙP and to remove byproducts. SC₀P–AuC and SC₁P–AuC were hexahedron-shaped nanomaterials composed of six porphyrin derivatives and a spherical AuC of ~1 nm in size. Their chemical compositions were Au₋₆₆(SC₁P)₋₆ and Au₋₆₆(SC₂P)₋₆.¹⁴ Fig. 2a and b show a TEM image of SC₀P–AuCs and the size distributions of the SC₀P–AuCs. The sizes of the AuCs were 1.9 ± 0.3, 1.2 ± 0.2 and 1.1 ± 0.1 nm for SC₀P–AuCs, SC₁P–AuCs and SC₂P–AuCs, respectively.¹⁴ The size of the SC₀P–AuCs is larger than that of the SC₁P–AuCs or SC₂P–AuCs. From the GPC chromatogram, the SC₀P–AuCs showed a peak at 17.0 min, which is 1.3 min faster than the peaks of SC₁P–AuCs and SC₂P–AuCs (18.3 min), indicating that the volume of SC₀P–AuC is larger than that of SC₁P–AuC or SC₂P–AuC (see Fig. S1 in ESI†). Furthermore, the peak shapes of the SC₀P–AuCs showed a Gaussian distribution indicating that the SC₀P–AuCs are highly monodispersed. These GPC results agreed well with the TEM observations. The larger SC₀P–AuCs can be explained by the rigidity of the SC₀P 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 SC₀P are rigid compared with SC₁P and SC₂P, a similar size-focusing effect was thought to be at work in the present case.

The Au core structure of a SC₀P–AuC was investigated by HAADF-STEM and by simulation using CrystalMaker (ver. 2.3.5). In the HAADF-STEM images of the SC₀P–AuC in the (110) zone axis, single-crystal or twinned face-centered-cubic (fcc) AuCs were observed (Fig. 2c). Twinned AuCs are attributed to the formation of small twinned Au cores after the reduction of Au¹⁺ 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

![Fig. 1](image1.png)

![Fig. 2](image2.png)
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 SC0P 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 SCnP molecules attached to a single AuC. UV-vis-NIR absorption spectrum of SCnP–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 SCnP–AuCs indicates that the SC0P–AuCs were highly monodispersed. Consequently, we propose that a major component of SCnP–AuC is a 14 porphyrin-coordinated Au1409 cluster in a face-on configuration as shown in Fig. 2d.

We also investigated how the large π–metal coupling affects the electronic state of SCnP on an AuC. Fig. 3a and b shows the absorption spectra of free SCnP and SCnP–AuCs. The absorption spectra of the SCnP–AuCs showed a decreasing absorbance from the visible to the NIR region and this is assigned to inter- and intraband absorption of the AuCs. For SCnP–AuCs, a localized surface plasmon band from 500 to 600 nm was observed owing to their larger diameter. Free SCnP exhibited Soret bands (S0 → S2 transition) at ~420 nm and four distinct Q bands (S0 → S1 transition) from 512 to 664 nm. On the contrary, the Soret bands of SCnP 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 × 105 to 3.2 × 104 M⁻¹ cm⁻¹), 9% (from 3.9 × 105 to 3.5 × 104 M⁻¹ cm⁻¹) and 38% (from 3.9 × 105 to 1.5 × 105 M⁻¹ cm⁻¹) for SC0P–AuCs, SC1P–AuCs and SC2P–AuCs, respectively. The peak positions of the Soret bands were red-shifted by 18 and 5 nm for SC0P–AuCs and SC1P–AuCs, respectively, while no red-shift was observed for the Soret band of SC2P on AuCs. The spectral change of SC0P on the AuCs was dramatic compared with SC1P and SC2P 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.3,4,6 and a closer approach induces a broadening of the energy levels because of π–metal coupling.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 SCnP on the AuC resembles that of the SC0P on the plasmonic Au nanoparticle (~10 nm),13 suggesting that the localized surface plasmon resonance and the electronic structure of Au core might not significantly influence the π–metal coupling.

The excited state behavior of the SCnP–AuCs was investigated by TA measurements because it provides important information about changes in density of state and molecule-metal interactions. Fig. 4a and b shows the TA spectra of free SCnP and SCnP–AuCs in DMF after excitation at 520 nm. Upon the excitation of free SCnP, a bleaching of the Q bands and a characteristic peak at ~1070 nm, which is assigned to the S1 state of the porphyrin were observed (Fig. 4a and c). The decreasing absorbance from 500 to 1000 nm quickly sharpened because of vibrational relaxation. Conversely, SC0P–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 (Fig. 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 S1 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”.29 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 SCnP–AuCs can be described as follows. Immediately after excitation, the SCnP–AuCs form an exciplex. An ultrafast charge separation proceeds from the exciplex (700 fs) and a recombination to the ground state (32 ps) occurs (Fig. 4c, see Fig. S2 in ESI for the decay profile†). Similar photoinduced behavior was reported for a porphyrin/fullerene system in a face-on configuration.22 TA spectra of SC1P–AuCs and SC2P–AuCs have not been obtained because of the current low stability of clusters when using lasers.24

![Fig. 3](Image)

**Fig. 3** UV-vis-NIR absorption spectra of (a) free SCnP and (b) SCnP–AuCs in DMF.

![Fig. 4](Image)

**Fig. 4** TA spectra of (a) free SCnP and (b) SCnP–AuCs in DMF after excitation using a 520 nm laser. (c) Energy diagrams of free SCnP and SCnP–AuC.
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 \( \pi \)-metal coupling exists between the porphyrin and the AuCs in the ground state, which results in the formation of an exciplex upon photo-excitation. This is the first observation of an exciplex between \( \pi \)-conjugated molecules and a pure metal. The SC_{0P}–AuCs are promising as Coulomb islands in SET because the tunneling voltage- and room temperature-driven SETs is in progress. The development of low voltage- and room temperature-driven SETs is in progress.

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Notes and references

1 M. L. Perrin, et al., Angew. Chem., Int. Ed., 2011, 50, 11223, see ESI†
6 G. Heimel, et al., Nat. Chem., 2013, 5, 187, see ESI†
18 The distances were determined by single-crystal X-ray diffraction for SC_{1P} and SC_{2P}. The structure of SC_{0P} was predicted by performing density functional theory calculation with the Perdew-Burke-Ernzerhof generalized-gradient approximation.
20 The formation of a charge transfer (CT) state causes a shift and broadening of the Soret band of the porphyrin.\textsuperscript{21} The image-charge effect and \( \pi \)-metal coupling might generate a CT-like state in the SC_{nP}–AuC. The CT-like state might contribute to the spectral changes.
24 Interfacial interactions in SC_{1P}–AuCs and SC_{2P}–AuCs are now under investigation by using TA and theoretical calculation, and will be discussed in a forthcoming paper.
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