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Gold nanocluster confined within a cage: template-directed formation of a hexaporphyrin cage and its confinement capability

Tomohiko Inomata and Katsuaki Konishi*

PRESTO, Japan Science and Technology Corporation (JST), and Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, North 10 West 5, Sapporo 060-0810, Japan. E-mail: konishi@ees.hokudai.ac.jp; Fax: +81-11-706-4538

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A novel container complex in which a 1.4 nm gold cluster is confined within a hexaporphyrin cage was synthesized; the cage showed notable confinement capability for the cluster core, but allowed the interpenetration of small molecules into the interstitial space.

Container complexes in which a molecule is encapsulated within a cage-like architecture have been of great interest in current chemistry, since the confined environment inside the cage provides unusual chemistry, *e.g.*, stabilization of highly reactive intermediates and creation of new stereoisomerism.[1,2] There have been many reports on such molecule-within-molecule systems, including those by self-assembly of several components, however the trapped molecules are mostly limited to organic compounds. We report herein a novel class of container system, in which an inorganic metal nanocluster is confined within an organic cage composed of metalloporphyrins.

Metal nanoclusters have attracted considerable attention recently in relation to their unique properties and potential applications for molecular devices and catalysts.[3,4] The cluster we chose here is a ligand-protected gold cluster with a 1.4 nm core, which was originally formulated as $Au_{55}(L)_n$ (Fig. 1) by Schmid and co-workers,[4c,5] and is characterized by the narrow size dispersity, high chemical stability,[6] and ease of modification with various thiolates.[7] The strategy for the cluster confinement involves intermolecular cross-linking among zinc porphyrins assembled around the cluster, for which the cluster modified with pyridine-appended thiolates (**1b**) was utilised. Thus, several zinc porphyrins were assembled over the cluster surface through the axial coordination of the outside pyridyl groups.

The synthesis started from the ligand exchange reaction of $Au_{55}(PPh_3)_{12}Cl_6$ (**1a**) with bis(4-pyridylmethyl)disulfide ($[SCH_2(4\text{-Py})]_2$), which gave $Au_{55}[SCH_2(4\text{-Py})]_{16}(PPh_3)_3$ (**1b**) in 88% yield.[8] As the zinc porphyrin monomer, we exploited zinc *meso*-tetraarylporphyrin (**2**, Fig. 1) with four terminal-olefin functionalities, by which the assembled porphyrin units were cross-linked *via* intermolecular olefin-metathesis (Scheme 1 (i)).[9] Typically, to a dry CH_2Cl_2 suspension (250 mL) of **1b** (250 mg, 17.8 µmol) was added **2** (96.7 mg, 108 µmol) and the mixture was stirred for about 30 min to give a homogeneous solution. To this solution was added Grubbs's second-generation ruthenium catalyst (**4**, 86.4 µmol),[9] and the reaction mixture, after stirring at room temperature for 12 h, was subjected to preparative exclusion chromatography (SEC). The brown fraction eluted first showed absorption bands characteristic of a pyridine-coordinated zinc porphyrin (430, 563, 604 nm) together with the overlapped broad absorption due to the gold-cluster moiety (Fig. 2a, c). On the other hand, the MALDI-TOF-MS spectrum (9-nitroanthracene matrix) showed a broad but significant peak centered at *ca.* 18700 (Fig. 2, inset), which is close to the sum of the formula weights of the original cluster (**1b**) (13607) and six zinc-porphyrin components (846 × 6 = 5076). In the infrared spectrum (KBr pellet), the C=C stretching bands due to the terminal olefin functionalities (1647 cm^{-1}), found in **2**, completely disappeared, indicating their consumption by the metathesis. Thus, this product is most likely to be a closed cage consisting of six zinc porphyrins in which **1b** is confined (**1b**@(**5**)$_6$). Accordingly, the calculated composition of **1b**@(**5**)$_6$ showed a good agreement with the result of the elemental analysis.[8] The yield, after precipitation with pentane, was 50% (170 mg) based on **2**, which is rather high considering that twelve coupling reactions among six molecules of **2** must occur to form a closed structure.

Interestingly, **1b**@(**5**)$_6$ was obtained, in the above SEC separation, as the sole product that contains both cluster and zinc porphyrin. The preferable formation of **1b**@(**5**)$_6$ appears to

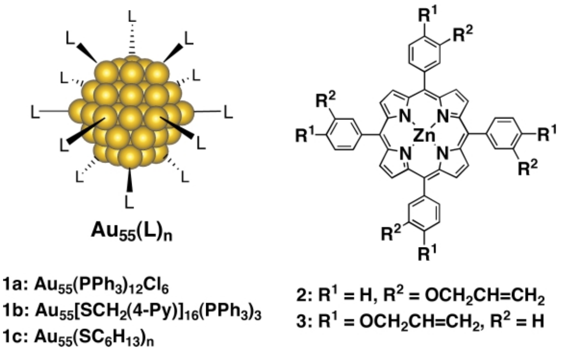
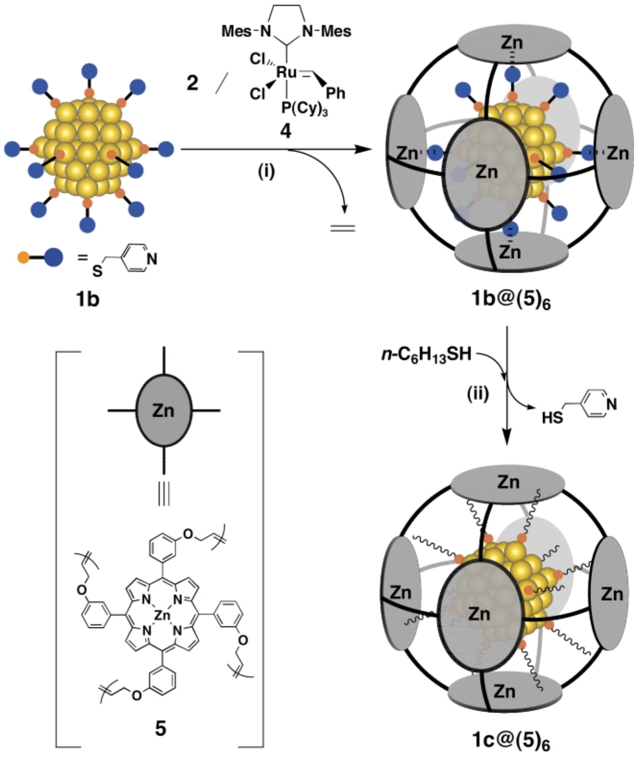


Fig. 1 Schematic structures of Au_{55} clusters and zinc porphyrins. For the gold cluster, one of the possible structures is shown.



Scheme 1

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be a result of the template effect of the cluster (**1b**),[10] since the cross-linking in the absence of the cluster occurred in a non-controlled fashion to give a mixture of several zinc-porphyrin oligomers. Model studies suggested that the cubic arrangement of six zinc porphyrins (**2**) around the cluster (**1b**) allows proximal orientation of the appended olefin functionalities. Thus, under the thermodynamic control associated with the kinetically labile coordination interactions, the formation of the hexaporphyrin cage may be favoured. In connection with this, it should be noted that the orientation of the olefin functionalities strongly affects the cage-closing process: When a regioisomer of **2** (**3**), bearing allyloxy groups at the *para* positions of the *meso*-aryl groups, was used as the porphyrin monomer, no caged products were obtained under otherwise identical conditions.

The ligand-exchange reaction of **1b**@(**5**)$_6$ with 1-hexanethiol, a nonfunctional thiol, in THF at room temperature proceeded smoothly to give a cluster 'floating' within the cage (**1c**@(**5**)$_6$) (Scheme 1 (ii)). **1c**@(**5**)$_6$ was brown in colour and its electronic absorption spectrum (Fig. 2b) was similar to that of the precursor **1b**@(**5**)$_6$ with a broad cluster absorption, but showed blue shifts of the bands due to the zinc-porphyrin cage (422, 552, 600 nm) as a result of the detachment of the pyridyl ligand. Analytical SEC showed a nearly unimodal peak, where the estimated molecular weight based on the polystyrene standards (1800) was much smaller than the formula weight, reflecting the compact sphere-like structure of **1c**@(**5**)$_6$. IR spectroscopy showed C–H vibrational bands at 2853 and 2922 cm^{-1} characteristic of the alkyl chains oriented on the cluster surface.[4d]

The facile conversion to **1c**@(**5**)$_6$ with the retention of the cluster confinement, thus observed, indicates that the cage has openings for the reversible interpenetration of small substrates (*e.g.*, 1-hexanethiol) into the inner space of the cage, but they are small enough to prevent the elimination of the confined cluster (Fig. 3). Actually, the cage of **1c**@(**5**)$_6$, though having no particular bonding links with the core, seems very reluctant to release the cluster even at high temperatures. For example, the absorption spectrum and SEC profile of **1c**@(**5**)$_6$, after being heated in refluxing *o*-dichlorobenzene (179 °C) for 2 h, were virtually identical to those before the heating. It should also be noted that **1c**@(**5**)$_6$ was stable towards halide anion that induces the aggregation of thiolate-protected gold clusters: When non-caged cluster (**1c**)[7a] was heated with an excess amount of tetramethylammonium bromide at 90 °C in *o*-dichlorobenzene, the solution colour turned from brown to blue within 30 min to show a plasmon absorption (540 nm) characteristic of large gold particles. In sharp contrast, under identical conditions, **1c**@(**5**)$_6$ showed no sign of such aggregation and retained the cluster confinement even after being heated for 5 h.

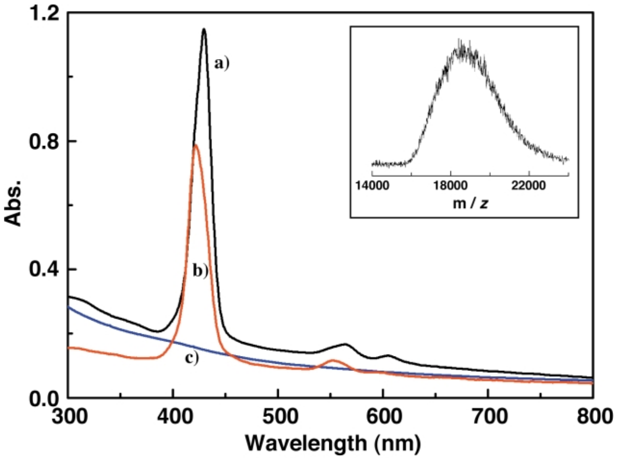

Fig. 2 Absorption spectra of a) **1b**@(**5**)$_6$ (black), b) **1c**@(**5**)$_6$ (red), and c) **1b** (blue) in CH_2Cl_2 at 25 °C. Inset: MALDI-TOF-MS spectrum of **1b**@(**5**)$_6$.

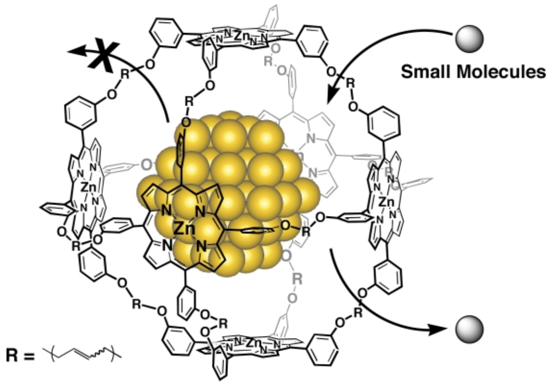

Fig. 3 Schematic representation of the hexaporphyrin cage confining a Au_{55} cluster (**1c**@(**5**)$_6$); surface ligands are omitted.

In summary, we have demonstrated the novel cage compound that confines a gold cluster. Unlike the functional clusters constructed by conventional surface-modifying methodology,[4] the present caged cluster has an interstitial space between the core and porphyrin shell, thereby allowing the access of small substrates to the central core through the openings of the cage. Considering also unique photochemical/electronic properties of metalloporphyrins and gold clusters and possible synergetic effects between them, the new hybrid architecture may have good potential for a variety of applications in materials science.

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8 The formulae represent the average compositions estimated from the elemental analyses. **1b**; anal. calc. for $C_{150}H_{141}Au_{55}N_{16}P_3S_{16}$: C, 13.24; H, 1.04; N, 1.65; S, 3.77%. Found: C, 13.76; H, 1.10; N, 1.46; S, 3.96%. MALDI-TOF MS (*m/z*) calc. 13607, found 13900 (br). **1b**@(**5**)$_6$; anal calc. for $C_{462}H_{357}Au_{55}N_{40}O_{24}P_3S_{16}Zn_6$: C, 29.70; H, 1.93; N, 3.00; S, 2.75. Found: C, 29.74; H, 2.41; N, 2.76; S, 2.99. MALDI-TOF MS (*m/z*) calc. 18685 found 18700 (br). ^{1}H NMR of these compounds were strongly affected by the gold cluster to show severely broadened signals (ref. 4).

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