

Synthesis and Photochemical Behavior of Platonic Hexahedron Composed of Six Porphyrins and an Au Cluster

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The structure of nanomaterial determines their individual properties and suprastructures they can form.^{1,2)} Therefore, it is very important to create the highly symmetric and size controlled nanostructure. However, precious control over size of metal clusters and conformation of protective ligands has been a challenging subject.^{3,4)} In this study, we report the synthesis of nano Platonic hexahedron composed of spherical Au clusters (AuCs) and six porphyrins derivatives through the face coordination of porphyrin derivatives on the AuCs.⁵⁾ The ground state interaction and excited state photochemical behaviour of these porphyrin face-coordinated AuCs will be also presented.

Two porphyrin derivatives, (tetrakis-5 α ,10 α ,15 α ,20 α -(2-acetylthiomethylphenyl) porphyrin (SC₁P) and tetrakis-5 α ,10 α ,15 α ,20 α -(2-acetylthioethyl phenyl) porphyrin (SC₂P) (Fig. 1), which have four acetylthio groups in the same direction against porphyrin ring were synthesized.⁶⁾ The AuCs coordinated by these porphyrin derivatives (SC_nP-AuCs) were synthesized by reduction of Au(III) in the mixed solvent (CH₂Cl₂ and CH₃OH) at 200 K in the presence of SC_nP. TEM observation revealed the formation highly monodispersed AuCs with sizes of 11.1 \pm 0.2 nm (SC₁P-AuCs) and 1.2 \pm 0.1 nm (SC₂P-AuCs). The GPC chromatogram of each SC_nP-AuCs showed the peak with Gaussian distribution, which indicates that the obtained SC_nP-AuCs are single components. The retention time of the SC₁P-AuCs is similar to that of the SC₂P-AuCs, which indicates that these two AuCs have similar volume. This result agreed with TEM observations. The MALDI-TOF-MS and ICP-AES measurements indicated that the composition of SC_nP-AuCs were Au₆₅(SC₁P)₆ and Au₆₆(SC₂P)₆, respectively. The most thermodynamically stable structure should have the lowest surface energy by completely covering the AuC surface. A Platonic hexahedron of six SC_nP is the only structure which completely cover the AuC surface by six porphyrin faces (Fig. 2). In addition, the center of each porphyrin ring should contact AuC to construct the Platonic hexahedron.

Interestingly, the intensity of Soret band for SC_nP on AuC decreased and red-shifted depending on the distance between the AuC and porphyrin ring, also inferring the face coordination of SC_nP on AuC and the strong interaction between AuC and SC_nP (Fig. 3).⁶⁾ This spectral shift indicates the strong ground state interaction between porphyrin rings and AuC. On the contrary, perpendicular system showed no interaction. The transient absorption measurement indicated that rapid charge transfer separation followed by recombination occurred from the singlet excited state of SC_nP to AuC, which is different behavior of perpendicular system.⁷⁾

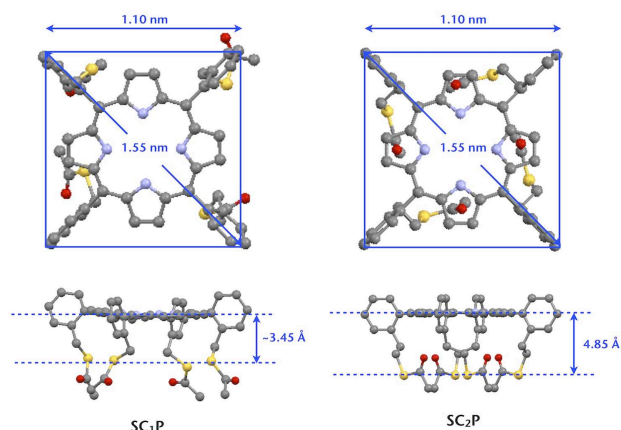


Fig. 1 Crystal structures of SC_nP ($n = 1, 2$).

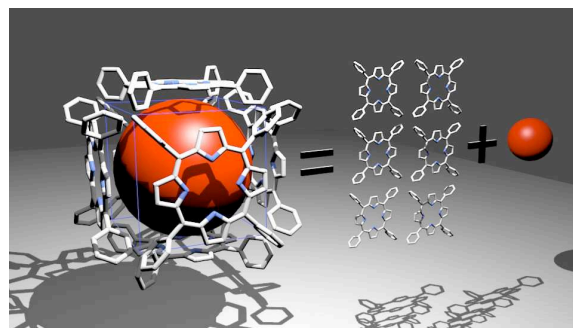


Fig. 2 Schematics of the SC_nP-AuCs constructed with six porphyrin faces and an inscribed Au sphere.

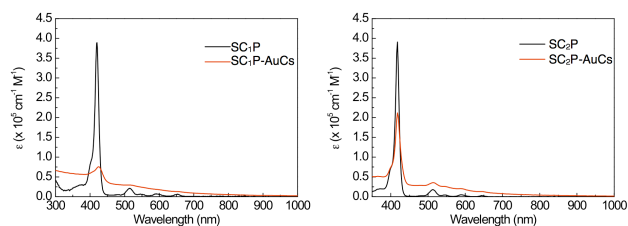


Fig. 3 UV-vis-NIR spectra for SC_nP and SC_nP-AuCs in DMF. The molar absorption coefficients were estimated from inductively coupled plasma atomic emission spectroscopy data.

References

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