VIII-J Designing Artificial Photosynthesis at Molecular Dimensions

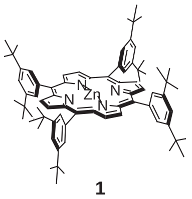
Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, and transition metal complexes. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

VIII-J-1 Photooxidation of Alcohols by a Porphyrin/quinone/TEMPO System

NAGATA, Toshi; ITO, Hajime; NAGASAWA, Takayuki

Photoinduced electron transfers involving porphyrins are widely studied, but utilizing the high-energy radical ion pairs for driving chemical reactions remains to be a great challenge. We reported preliminary results on photooxidation of alcohols by a porphyrin/quinone/TEMPO system in AR2002. This year we report the mechanistic detail of this reaction system.

When a solution of porphyrin **1** (1 μmol), TEMPO (25 μmol), 2,5-di-*tert*-butyl-1,4-benzoquinone (100 μmol), benzyl alcohol (300 μmol) and *n*-dodecane (50 μmol; an internal standard for the gas chromatography) in 0.5 ml of dry pyridine was irradiated with visible light ($\lambda > 500$ nm), benzaldehyde was formed with concurrent formation of 2,5-di-*tert*-butyl-1,4-hydroquinone. The substrate dependence experiments revealed following order of reactivity: benzylic ≈ allylic > primary >> secondary (no reaction). This is in accordance with other reported TEMPO-mediated oxidation.



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With benzyl alcohol as a substrate, the initial rates of product formation were examined under various conditions (Figure 1). As shown in parts (a) and (b), the rate increases with increasing concentrations of PhCH$_2$OH and TEMPO. Particularly interesting is the dependence on the quinone concentration, shown in part (c). Here the initial rates decrease with increasing quinone concentration. The dependence on the porphyrin concentration (part (d)) also shows a similar trend.

The negative dependence on quinone concentration can be explained by considering the quantum yields of the triplet radical pairs. When the concentration of quinone becomes higher, the quantum yield of the triplet radical pair is lowered because the singlet state is more likely to be quenched prior to intersystem crossing. On the other hand, the negative dependence on porphyrin concentration is ascribed to the electron-transfer equilibrium between the porphyrin cation radical and TEMPO (Equation 1). As the concentration of porphyrin becomes higher, the equilibrium is pushed to the left and the steady-state concentration of the oxoammonium cation TEMPO$^+$ becomes lower. The proposed reaction mechanism is shown in Scheme 1.

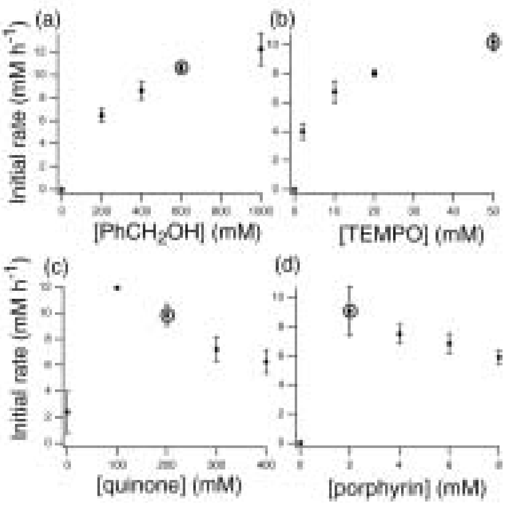
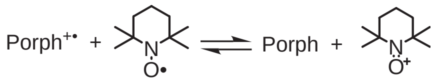
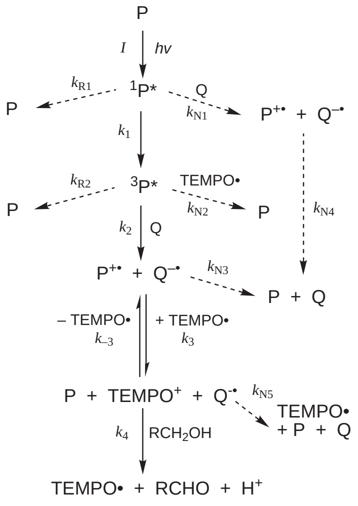


Figure 1. The initial rates of formation of PhCHO under various conditions.



Equation 1.



Scheme 1. Proposed reaction mechanism.

VIII-K Development of New Nanomaterials as Components in Advanced Molecular Systems

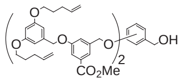
Nanometer-sized materials exhibit unique electronic behavior. In the quest of advanced redox catalysis, we are currently interested in combining nanometer-sized materials into molecular redox systems. Herein we report two attempts to develop new nanomaterials that potentially suit for combination with advanced molecular system.

VIII-K-1 Development of New Spatially-Relaxed Dendrimers and Their Application as Precursor to Redox Pool Molecules

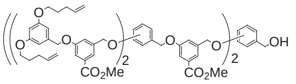
KIKUZAWA, Yoshihiro; NAGATA, Toshi

We synthesized a series of new dendrimers with up to fourteen "internal" carboxyl groups. These dendrimers (**G$^{1-3}$**) are made from a branching unit and a spacer unit with a carboxyl group. Introduction of the spacer groups makes the internal carboxyl groups more spatially relaxed than previously reported dendrimers.

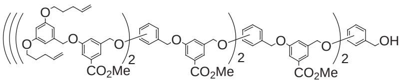
This type of dendrimer was used as a building framework of new redox pool molecules. The dendrimer **G^3** was connected to a porphyrin, the internal carboxyl groups were converted to alcohols, and ferrocene-carbonyl groups were introduced via ester linkages to give **P-G^3(Fc)$_{14}$**. This molecule will be useful for examination of photoinduced electron transfer between a porphyrin and multiple electron donor molecules.



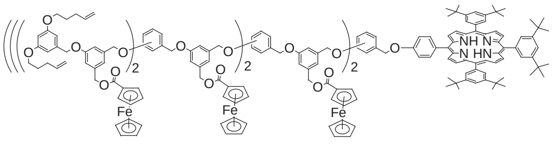
G^1



G^2



G^3



P-G^3(Fc)$_{14}$

VIII-K-2 Synthesis and Size Control of Gold Sub-Nanoparticles Stabilized by Tripod Organic Molecules

HOSOKAWA, Youichi; NAGATA, Toshi

Recently, gold nanoparticles have received much attention as potentially useful materials showing novel electronic, optical, optoelectronic, and magnetic properties derived from the quantum size effect. One promising application of these materials is utilization as one of the functional "components" in molecular systems. To realize this idea we are developing techniques to treat metal nanoparticles as if they were "molecules."

We synthesized new tripod molecule **1**–**3** (Figure 1) and examined stabilization of of gold sub-nanoparticles stabilized by them. These molecules are designed so that a single molecule can enclose a single metal nanoparticle to give a "molecular" nanoparticle complex (Figure 2). The multi-point interaction by arylthioether units will produce the stabilization, and the different "leg" length will also result in size-selection of metal nanoparticles. Figure 3 shows the TEM pictures and the observed diameter distribution of gold nanoparticles derived from **1**–**3**. The most frequent values of the diameter distribution became larger with increasing numbers of the benzyl thioether units.

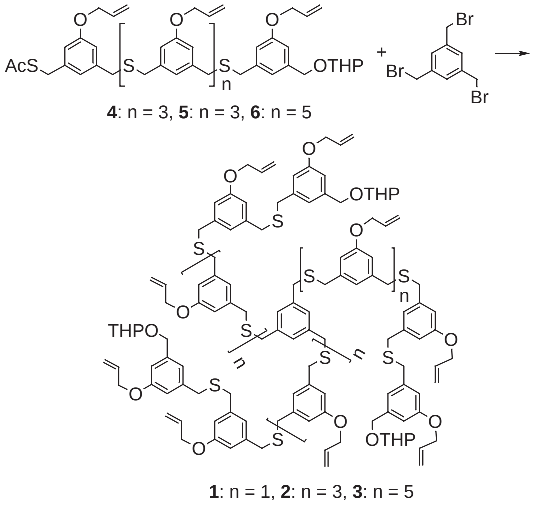


Figure 1. Preparation of the tripod molecules **1**–**3**.

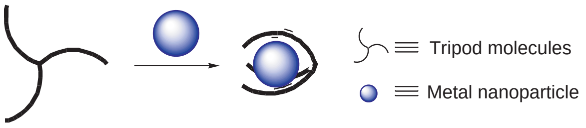


Figure 2. A schematic representation of the complex between the tripod molecule and the metal nanoparticle.

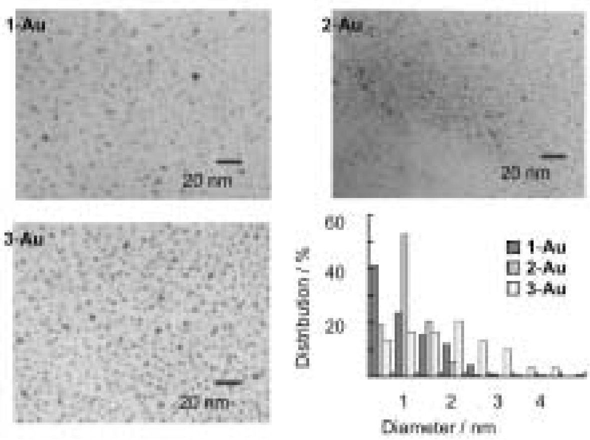


Figure 3. TEM images and the diameter distribution of **1**-, **2**-, and **3-Au**.