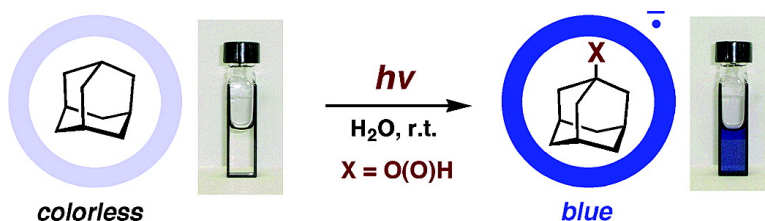


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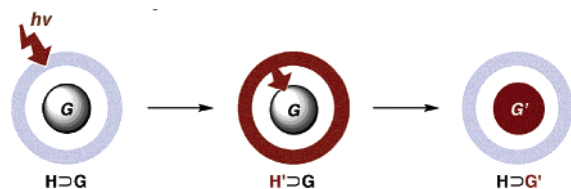


Alkane Oxidation via Photochemical Excitation of a Self-Assembled Molecular Cage

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Photoinduced energy and electron transfer between self-organized molecules is an essential and the most important process in plant photosynthesis that in turn favors all living things.¹ Complexity and elegance lying in the photosynthetic system have fascinated and stimulated chemists to translate the complexity into simplicity in model systems.² As in nature's system, therefore, molecular assemblies that experience photoexcitation and subsequent intermolecular energy/electron transfer highly promise the development of photodriven molecular systems from artificial photosynthesis models to solar cells, photo sensors, and photo reactors.^{1–3} Discussed in this communication is a self-organized host–guest complex where none of the components is photochemically active, yet the assembly of the components efficiently promotes the photochemical oxidation of inert guests. The overall process involves (i) the accommodation of an inert guest (**G**) in a self-assembled host (**H**), (ii) the photochemical excitation of the host framework, and (iii) the subsequent oxidation of the guest within the cavity, as schematically shown below. Although there are several examples for chemical reactions within self-assembled cages and capsules,^{4,5} the result shown here provides the first example of a chemical reaction that is sensitized by a self-assembled cage.



The host compound we deal with here is an M_6L_4 -type coordination cage (**1**), which self-assembles from six Pd^{2+} coordination blocks and four pyridine-based bridging ligands.⁶ It has strong absorption at <370 nm, and the ligand should behave as a strong electron acceptor because of electron donation to Pd^{2+} centers at three pyridine coordination sites. Recently, we have revealed that neutral organic molecules are strongly encapsulated in cage **1** and that the reactivities of the guest molecules are controlled by the cavity.⁷ In particular, stereochemical course in the $[2 + 2]$ photodimerization of olefins is strictly controlled in the cage.⁶ In this photoreaction, however, the cage does not participate in the photochemical processes but provides only confined microspace to control the reactions.

To explore the intrinsic photoresponsible nature of coordination cage **1**, we examined the photoexcitation of the cage itself accommodating inert alkane guests. When adamantane-encapsulated complex $1 \supset (2)_4$ (**2**: adamantane) was irradiated under aerobic conditions, we found the regioselective oxidization of **2** at a tertiary carbon. An aqueous solution of $1 \supset (2)_4$ complex (5.0 mM) (Figure

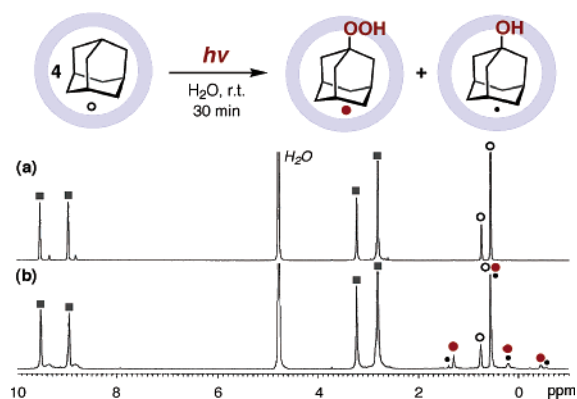
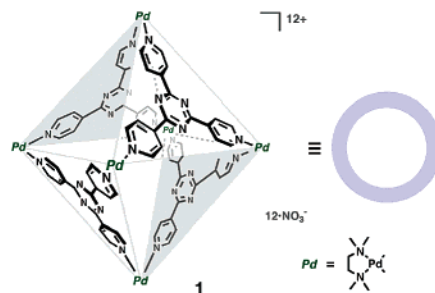


Figure 1. NMR observation of the photooxidation of adamantane (**2**) within cage **1** (500 MHz, room temperature, D_2O , TMS as external standard). (a) An aqueous solution of $1 \supset (2)_4$. (b) The reaction mixture after irradiation for 30 min under air.

1a) was prepared by suspending powdered **2** in D_2O solution of cage **1** and irradiated by a high-pressure mercury lamp in a Pyrex tube at room temperature for 30 min under air. After irradiation, the 1H NMR spectrum showed new signals (Figure 1b) which were deduced to 1-adamantyhydroperoxide and 1-adamantanol, the total yield of which was estimated to be 24% (or 96% assuming that only one guest is oxidized per cavity). The ratio peroxide/alcohol = 4:1.⁸



The host–guest complexation is essential to the photooxidation of **2**, because **2** remained intact in the absence of cage **1** or in the presence of only the metal or the ligand component of cage **1**. Cyclic alkanes (C_nH_{2n} , $n = 6–8$) were also photooxidized to give corresponding hydroperoxides and ketones in reasonable yields. Larger cyclic alkanes (e.g., decalin and perhydrofluorene) and linear alkanes were not accommodated by the cage and, hence, not oxidized upon irradiation. Tight host–guest contact seems very important because a related M_6L_4 bowl-shaped host⁷ with an open cavity did not mediate the photooxidation of the alkane guests under the same conditions, although the host accommodated the guest. In fact, the X-ray crystallographic analysis of $1' \supset (2)_4$ complex (**1'**: an analogue of **1** where N,N,N',N' -tetramethylethylenediamine is replaced by 4,4'-bipyridine) revealed the close aggregation of

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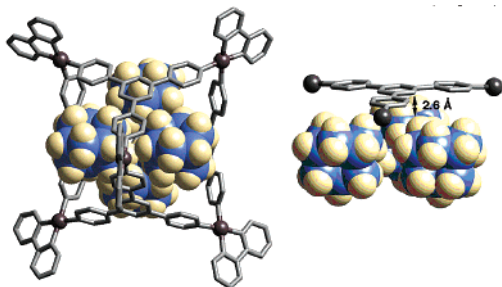


Figure 2. Left: Crystal structure of $1'(2)_4$ complex. Right: A partial structure showing the close contact (2.6 Å) between a ligand and three guests.

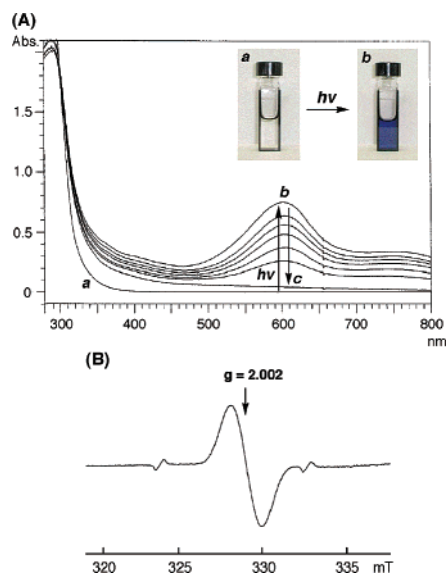


Figure 3. (A) UV-vis spectra of the aqueous solution of $1'(2)_4$ at room temperature. (a) Before photoirradiation. (b) After photoirradiation for 30 min under argon; color decay after the irradiation at 1, 4, 8, 18, and 24 h (each line). (c) After exposure to air. (B) ESR spectrum (H_2O , $-170\text{ }^\circ\text{C}$, MnO as external standard) of $1'(2)_4$ after photoirradiation for 30 min under argon.

four adamantane molecules within the cavity of $1'$ with $\text{C}-\text{H}\cdots\pi$ (guest–host) distances being shorter than the sum of van der Waals radii (Figure 2).⁹

Under anaerobic conditions, we observed an unusual color change of the aqueous solution of $1'(2)_4$ by photoirradiation. When the solution of $1'(2)_4$ (2.0 mM) was irradiated under argon, the colorless solution quickly turned blue (Figure 3A: $a \rightarrow b$).¹⁰ UV-vis spectrum of the blue solution showed a strong absorption band at $\lambda_{\text{max}} = 593\text{ nm}$ ($\epsilon = 9300\text{ M}^{-1}\text{ cm}^{-1}$ based on 1), which reached maximum in 30 min. The ^1H NMR spectrum of the solution revealed the formation of 1-adamantanol. The blue species generated from $1'(2)_4$ by the irradiation is so stable under argon as to remain unchanged for more than 3 days at room temperature. However, the solution immediately turned colorless by exposing it to oxygen (or air) (Figure 3A: $b \rightarrow c$). The same species seems to be generated in solid state since the crystal of $1'(2)_4$ also turned blue upon irradiation. ESR analysis of the blue solution and the solid showed a broad signal ($g = 2.002$) at both $20\text{ }^\circ\text{C}$ and $-170\text{ }^\circ\text{C}$ (frozen solution), indicating the generation of radical species (Figure 3B).

Interestingly, the radical species is not generated upon the irradiation of an empty host or a host–guest complex with aromatic guests (e.g., benzene and naphthalene) that are not oxidized under the conditions. Obviously, the radical formation and the guest oxidation are not independent but simultaneous processes.

To clarify the mechanism for the guest oxidations and the radical formation, we examined some control experiments. Exchange of counterion (from NO_3^- to PF_6^-), metal (from Pd^{2+} to Pt^{2+}), and/or solvent (from H_2O to MeCN) did not affect the photoreaction, while the replacement of a triazine core of the ligand by a benzene core suppressed the photoreactivity. Thus, the radical should generate not on the counterions, metals, or solvents but on the triazine ligand. ^{18}O -labeling on O_2 or H_2O resulted in the incorporation of ^{18}O in the oxidized products, suggesting that the reaction should involve adamantyl radical, which is subsequently trapped by O_2 or H_2O . On the basis of these results, we propose the following sequential steps for the reaction mechanism: (i) photochemical excitation of cage 1 at the triazine ligand, (ii) electron transfer from a close-contacted adamantane guest to the cage host, giving rise to a pair of 1-adamantyl radical (plus H^+) and radical anion of 1 , and (iii) the former is immediately trapped by O_2 (in the aerobic conditions) or H_2O to give the oxidized products, while the latter is stable enough under anaerobic conditions but rapidly quenched with O_2 under aerobic conditions.

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Supporting Information Available: Experimental details and spectroscopic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Crystal data for $1'(2)_4$: $\text{C}_{172}\text{H}_{160}\text{N}_{48}\text{O}_{36}\text{Pd}_6$, $M = 4108.64$, tetragonal, space group $P4_32_12$ (no. 96), $a = b = 29.579(6)\text{ Å}$, $c = 33.202(9)\text{ Å}$, $V = 29049(11)\text{ Å}^3$, $T = 78(2)\text{ K}$, $Z = 4$, $D_c = 1.123\text{ g cm}^{-3}$, λ (Mo $K\alpha$) = 0.71073 Å , 339 602 reflections measured, 33 392 unique ($R_{\text{int}} = 0.1598$) which were used in all calculations. The structure was solved by direct method (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1487 parameters. $R_1 = 0.1109$ ($I > 2\sigma(I)$) and $wR_2 = 0.2844$, GOF 1.016; max/min residual density 1.081/−0.853 e Å^{-3} . CCDC reference number 233 338.
- (10) The photooxidation of cyclic alkenes within 1 was also accompanied by the same color change under argon.

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