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High Catalytic Activity of Manganese–Porphyrin Cage Confining a Metal Nanocluster in Styrene Epoxidation

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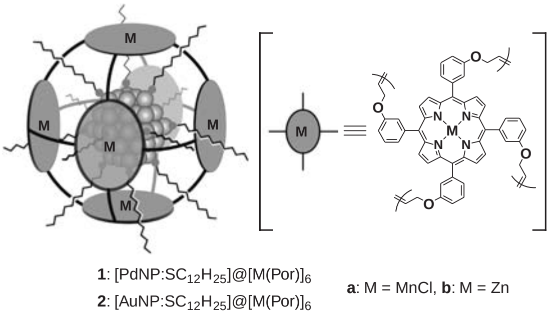
Mn–porphyrin cages confining ca. 1.4–1.5 nm Pd and Au clusters (**1a** and **2a**) showed high catalytic turnover numbers rather than simple monomeric porphyrin complex (**3a**) in styrene epoxidation by iodosobenzene. Absorption spectroscopic studies indicated that the accumulation of inactive species is efficiently suppressed when the cage catalysts **1a** and **2a** were employed.

Since the Haruta's discovery of prominent catalytic activity of Au nanoparticles of 1–3 nm diameters,[1] there emerged a considerable interest in the catalysis of small metal nanoclusters in this size regime.[2,3] Recently, we have succeeded in the synthesis of a hexaporphyrin cage confining a single 1.4 nm Au cluster (Au_{55}).[4] Herein, we report that the Mn–porphyrin cages confining Pd (**1a**) and Au (**2a**) clusters exhibit high catalytic activities in styrene epoxidation with iodosobenzene (Figure 1).

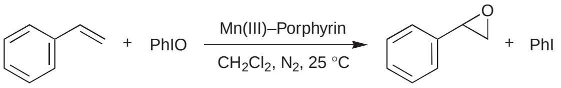
The cage of Zn–porphyrin hexamer that confines a dodecanethiolate-coordinated Pd cluster (**1b**) was synthesized according to our previously reported protocol of the Au cluster analogue (**2b**).[4] Thus, several allyloxy-appended zinc tetraphenylporphyrins assembled around a 4-pyridylmethylthiolate-ligated Pd cluster ($d \approx 1.5$ nm)[5] were cross-linked by Grubbs olefin metathesis. The ligand exchange of the linking thiolates with dodecanethiolate followed by repeated purification by Bio-beads SX-1 chromatography afforded **1b** in 25% yields.[6] The Zn–porphyrin units of **1b** and **2b** were demetalated by treatment with TFA followed by metalation with $Mn(OAc)_2$ according to a standard method (in DMF at 80 °C then washing with brine) to give chloromanganese(III)–porphyrin cages confining the clusters (**1a** and **2a**). Similarly to the Zn precursors (**1b** and **2b**), the absorption spectra of **1a** and **2a** were approximately sum of the absorptions of manganese–porphyrin and metal clusters, indicating the absence of electronic interaction between the two components.



1: $[PdNP:SC_{12}H_{25}]@[M(Por)]_6$
2: $[AuNP:SC_{12}H_{25}]@[M(Por)]_6$

a: M = MnCl, **b**: M = Zn

Figure 1.



Scheme 1.

Catalysis of the cluster-confining Mn–porphyrin cages (**1a** and **2a**) was investigated in styrene epoxidation by iodosobenzene (PhIO) (Scheme 1), where Mn(TPP)Cl (TPP: tetraphenylporphinato) (**3a**) was used as a monomeric control. Typically, to a CH_2Cl_2 solution (2 mL) of the catalyst ($[\text{Mn porphyrin}]_0 = 90\,\mu M$), styrene (450 mM), internal standard (naphthalene, ca. 30 mg), and PhIO (90 mM) were successively added at 25 °C under N_2, and the reaction progress was monitored by GC. It is well known that Mn(III)–porphyrin forms Mn(V)=O species as a reactive intermediate to catalyze this reaction, but its turnover capability is generally low due to the inactivation by irreversible ligand oxidation and Mn(IV) complex (e.g., μ-oxo dimer) formation during the catalytic cycle.[7,8] Actually, the reaction catalyzed by **3a** showed a sharp rise of the turnover number (TON; $[\text{styrene oxide}]/[\text{Mn–porphyrin}]_0$) in the initial several minutes but thereafter proceeded very slowly to give after 10 h a turnover number of 160 (16% yield) (Figure 2(○)). In contrast, when the Mn–porphyrin cage confining a Pd cluster (**1a**) was used as a catalyst at the same Mn concentration, the reaction proceeded much faster to show a steady formation of styrene oxide (●), where the TON number after 10 h was approximately 3.5 times larger (ca. 580) than that observed with monomeric **3a**. On the other hand, the caged Pd cluster, which possibly serves as another catalytic center, was essentially catalytically inert; neither of dodecanethiolate-ligated Pd cluster ($PdNP:SC_{12}H_{25}$, $d \approx 1.5$ nm) nor the Zn–porphyrin analogue of **1a** (**1b**) promote the styrene oxidation by PhIO. Furthermore, the presence of the Pd cluster in the **3a**-catalyzed reaction system did not cause substantial effects on time courses of the reaction (◆).

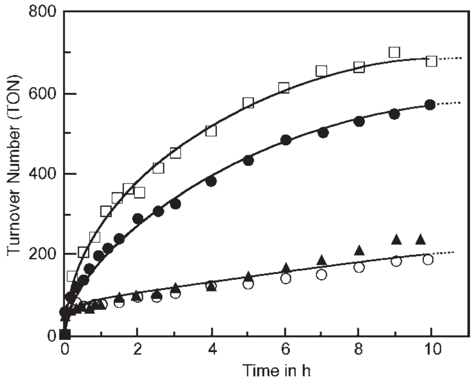


Figure 2. Time courses of the reaction of styrene (450 mM) with PhIO (90 mM) in the presence of 90-μM Mn–porphyrin catalyts; **1a** (●), **2a** (□), **3a** (○), **3a**/$PdNP:SC_{12}H_{25}$ (90/15 μM, ◆) in CH_2Cl_2 at 25 °C.

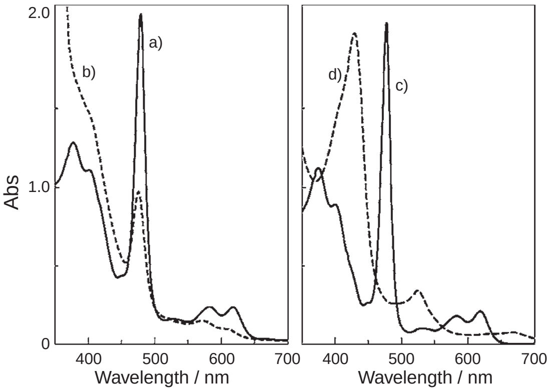


Figure 3. Absorption spectra in CH_2Cl_2 at 25 °C of **1a** (a), **3a** (c), and the filtrated reaction mixtures of **1a** (b) and **3a** (d) after 10-h reaction under the conditions in Figure 2.

As for the effect of the metal element constituting the cluster, the use of a Au cluster of a similar size (**2a**), which alone is also catalytically inactive for this epoxidation reaction, also resulted in a similar enhancement of the catalytic activity (□). The reaction was faster than the Pd analogue (**1a**), where the TON after 10 h was 4.1-times larger (ca. 650) than that observed with monomeric **3a**.

In contrast to the remarkable difference of the TONs, the initial rates of the above four reaction systems seem almost similar to each other (Figure 2), suggesting that the cage structure and the presence of the proximal cluster hardly affect the inherent reactivity of the Mn catalysts under this reaction condition. Therefore, it is likely that the high TONs observed for the cage catalysts (**1a** and **2a**) are associated with the extension of the catalyst lifetimes. In connection with this, we measured absorption spectrum of the reaction mixture in order to investigate the dominant species under reactive conditions. As shown in Figure 3, either of **1a** and **3a** before the reaction gave absorptions at 478, 583, and 619 nm due to the monomeric Mn(III)–porphyrin complex (Figures 3a and 3c). However, the spectral profiles after 10-h reaction were evidently different from each other: When the reference catalyst (**3a**) was used, the original bands were completely disappeared, while new bands were observed at 430, 525, and 666 nm (d) where the spectral profile was very similar to that reported for the catalytically inactive Mn(IV)–porphyrin.[9] On the other hand, with the cage catalyst (**1a**), the original absorptions obviously survived, where no sign of formation of the inactivated species was detected (b). Thus, the monomeric catalyst (**3a**) easily loses the activity under reactive conditions, while such an inactivation process hardly takes place for the cage catalysts (**1a** and **2a**) whereby they can retain the activities for a long time.

It has been claimed that one of the inactivated Mn(IV) species of **3a** is oxo-bridged dimer.[7,8] The formation of such a dimeric complex may be hampered with the cage catalysts by the conformational rigidity of the porphyrin units. Thus, the limited flexibility of the porphyrin skeletons, owing to the presence of the stuffed thiolate-coordinated cluster within the cage, may not allow the ring distortion required for the dimer formation.[10] On the other hand, it should be also noted that the two cage catalysts confining Pd (**1**) and Au (**2**) clusters showed different catalytic courses. This definite difference suggests that the metal-cluster units are involved in the catalytic process. In this respect, one possibility is that the proximal clusters promote the oxidation of transiently formed inactive Mn(IV) complex to regenerate active Mn(V) species, taking also account of the recent reports of the oxidation capability of these clusters.[2,3,11] Further studies on the role of the metal clusters in the catalytic cycles are currently under way.

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