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[9] Crystal structure data for $(\mathbf{1a})_2(ReO_4)_2$: $C_{88}H_{112}Cu_4N_8O_8Re_2S_{16}$, $M_r = 2549.37$, monoclinic, space group $P2_1/c$, $a = 16.096(23)$, $b = 26.620(35)$, $c = 32.039(41)$ Å, $\beta = 90.89(1)^\circ$, $V = 13726$ Å^3, $Z = 4$, $\rho_{calcd} = 1.234$ gm cm^{-3}. Data were measured on a Marresearch Image Plate system using $Mo_{K\alpha}$ radiation with the crystal positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 10 mins. 12787 reflections were measured to give 8069 independent reflections (R(int) = 0.0327). Data analysis was carried out with the XDS program.[13] The structure was solved using direct methods with the SHELX86 program.[14] The Re, Cu, and S atoms were refined with anisotropic thermal parameters. The ReO_4 anions had high thermal motion, but no disordered model proved satisfactory. The crystal was twinned (hkl, $hk - l$) with a refined factor of 0.23(2). An absorption correction was introduced using DIFABS.[15] Distance and thermal constraints were used particularly for the alkyl chains. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using SHELXL.[16] The final R values were $R1 = 0.1094$ and $wR2 = 0.3018$ for 4572 data with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166825. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[10] The observation of a room temperature magnetic moment a little higher than that usually observed for a free copper(II) ion (1.7–1.9 B.M.) may be attributed to either a small quantity of $FeCl_4^-$ co-crystallizing and occupying ReO_4^- sites in the unit cell or incomplete oxidation of the catenane.
[11] We chose to follow the emergence of the tricationic peak because ions arising from the dication catenane (for example, $(\mathbf{1a})_2^{2+}$) overlap with the monocation of the ring (for example, $(\mathbf{1a})^+$), and similarly, the tetracation of the catenane (for example, $(\mathbf{1a})_2^{4+}$) overlaps with the signal for the dication of the ring (for example, $(\mathbf{1a})^{2+}$).
[12] Evidence for the lability of the copper(III) oxidation state in the dithiocarbamate complex comes from the mixing of simple copper(III) alkyldithiocarbamates which leads to global exchange of the alkyldithiocarbamate ligands, as evidenced by electrospray mass spectrometry, see A. M. Bond, R. Colton, A. D. Agostino, J. Harvey, J. C. Traeger, *Inorg. Chem*. **1993**, *32*, 3952.
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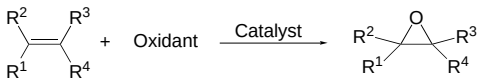
Artificial Enzymes Formed through Directed Assembly of Molecular Square Encapsulated Epoxidation Catalysts**

Melissa L. Merlau, Maria del Pilar Mejia, SonBinh T. Nguyen,* and Joseph T. Hupp*

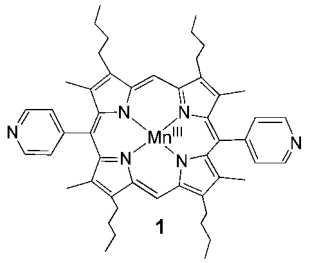
Enzymes are exquisite catalysts for chemical and biochemical reactions: They typically display excellent stability and are highly selective both with respect to the substrates used and the products produced. Most enzymes are comprised of a highly potent catalytic center and a surrounding protein superstructure. In contrast to many, or most man-made, catalysts, naturally occurring enzymes tend to rely upon the superstructure, rather than the catalytic site itself, to achieve substrate selectivity. In addition, the superstructure serves to isolate the catalytic center from other reactive centers, thereby enhancing the center's stability and extending its functional lifetime. Here we describe the artificial enzyme-like induction of stability and selectivity for a simple epoxidation catalyst by a supramolecular coordination chemistry approach. We further show that the selectivity is tailorable through the supramolecular approach. The tailorability permits, in principle, the rapid and systematic optimization of catalytic selectivity for specific substrates.

To demonstrate the utility of the encapsulation concept we targeted the epoxidation of olefins [Eq. (1)] because of its



(1)

relevancy in biooxidation.[1] We stress that our goal here is to demonstrate the utility of directed supramolecular complex formation in manipulating the properties of conventional catalysts rather than to create a competitive analogue of existing epoxidation catalysts.



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The baseline for comparing catalyst stability was established by using **1**

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(MnDPyP), which was synthesized by the adaptation of published methods.[2, 3] The alkyl groups surrounding the porphyrin framework provide needed solubility in reaction solutions, while the pyridyl groups are essential to the supramolecular assembly process described below. Many variants of simple manganese porphyrins have previously been examined as epoxidation catalysts[4–6] as a result of their high functional and structural similarity to the iron heme moiety comprising the catalytic center of cytochrome P450, a naturally occurring enzyme used in the oxidative metabolism of many biological compounds.[7] The naked manganese porphyrin, like the iron heme mimics, degrades fairly rapidly under catalytic reaction conditions (for example, there is a complete loss of activity after about 50 catalytic cycles). The primary mode of catalyst deactivation under the conditions used is through the formation of an oxo-bridged (Mn-O-Mn) dimer,[8] although some degree of parallel degradation through ligand oxidation cannot be ruled out.

By analogy to the protein superstructure employed by the iron heme in the active cytochrome, we encapsulated catalyst **1** in a supramolecular cavity by using a directed-assembly approach[9] to impart both stability and reaction selectivity (Figure 1). This approach is in contrast to the related method of generating catalyst protection and selectivity enhancement by creating a catalytic cavity using sophisticated and technically challenging covalent chemical modification strategies.[10]

We made use of a large preorganized, porphyrin-derived cavity structure[11] (**2**; itself obtained through coordinative directed assembly) with Lewis acidic receptor sites (Zn^{II}), and a catalytic center (**1**) with peripheral Lewis bases (pyridyl groups; Scheme 1). In the presence of equal or excess amounts of **2**, optimal complex formation is achieved through coordinative directed assembly such that **1** bisects the cavity and doubly binds to the cavity's walls with an association constant of approximately $10^6\,\text{M}^{-1}$ in dichloromethane.[12] Once the catalytic center is encapsulated it cannot attack a similarly encapsulated catalyst or the molecular square framework. At the same time, however, the roughly 9×18 Å "half-cavity" defined by [**1**+**2**] is large enough to permit many olefinic substrates to reach the catalytically active manganese center. In fact, concentration of olefins within the cavity is expected to be high since there is evidence for the preferential binding of aromatic substrates in molecular square cavities.[13, 14] This is thus an ideal scenario for the induction of enhanced catalyst stability, as measured by the increase in catalyst lifetime and by the number of catalytic cycles (turnovers) per manganese reaction center.

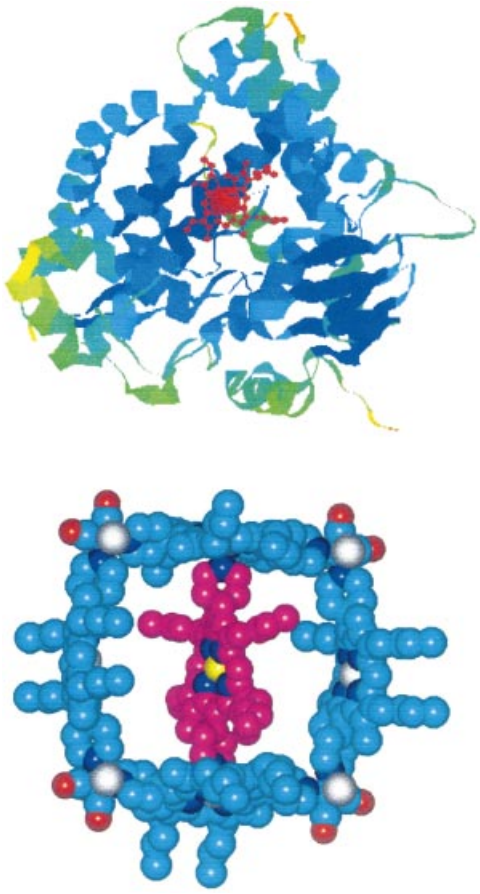
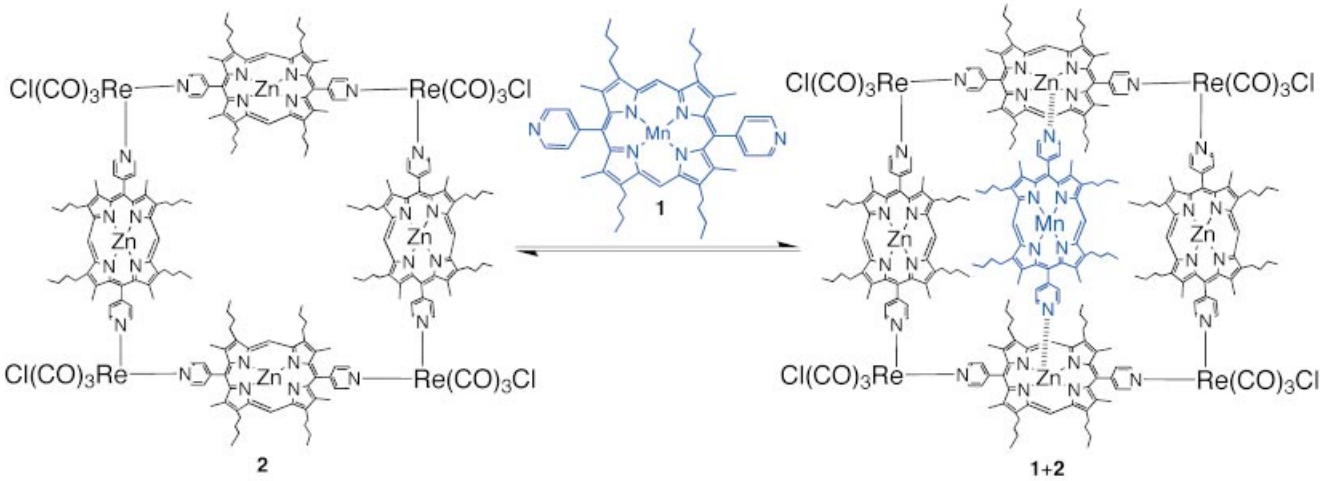


Figure 1. The conceptual topological similarity of cytochrome P450[23] and a supramolecular encapsulated catalyst assembly ([**1**+**2**], see text for more information).

Styrene epoxidation using millimolar solutions of **1** and the supramolecular complex **2** revealed a tenfold increase in the



Scheme 1. Encapsulation of epoxidation catalyst **1** with complex **2** by directed assembly.

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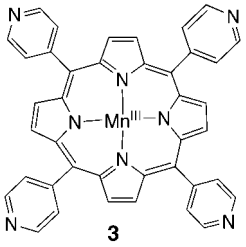
turnover number (TON) following complex formation.[15] In addition, the catalyst lifetime under reactive conditions was extended from approximately ten minutes to greater than three hours by protective encapsulation.[16] A quantitative consideration of the formation of the supramolecular complex shows that approximately 3% of the catalyst will remain unbound when millimolar concentrations of catalyst and **2** are used. The dynamic equilibrium between bound and unbound catalyst could account for the observed eventual destruction of all of the catalyst after three hours. Consistent with this interpretation, replacement of **1** by the even more strongly complexed catalyst *meso*-tetra(4-pyridyl)porphinatomanganese(III) chloride (**3**, K_b ca. $10^7\,M^{-1}$) greatly enhances functional stability, and results in TONs of approximately 1500.[17] Conversely, weaker binding complexes result in fewer catalyst turnovers.[8]



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Since both the above-mentioned catalyst degradation pathways are bimolecular in the catalyst itself, intentional dilution of the catalyst should also enhance its stability. We find that diluting catalyst **1** by a factor of 1000 while retaining the concentration of **2** at the millimolar level (in order to preserve supramolecular association) further improves the stability such that turnover numbers reach nearly 7000 in the case of **2** and 21000 in the case of **3** (Figure 2). Thus, the functional stability of more-or-less conventional catalysts can be enhanced 10- to 100-fold through formation of a supramolecular complex.

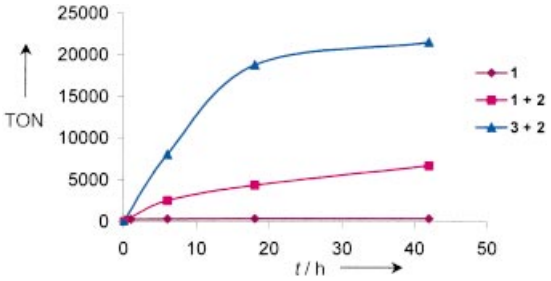
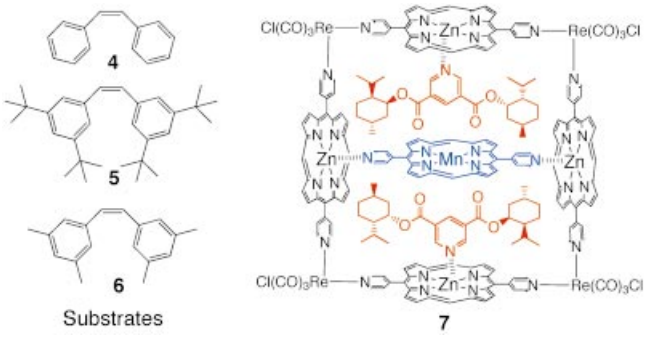


Figure 2. The enhanced stability and enhanced TONs of the catalyst assemblies [**1**+**2**] and [**3**+**2**] compared to the free catalyst **1**.

Formation of the supramolecular complex and catalyst encapsulation also engenders reaction selectivity. For example, competitive epoxidation reactions with both *cis*-stilbene (**4**, Scheme 2) and *cis*-3,3′,5,5′-tetra-*tert*-butylstilbene (**5**) as the substrate showed that the sterically more encumbered **5** is 3.5 times less reactive with [**1**+**2**] than with the naked catalyst. The difference is attributed to partial exclusion of **5** (on the basis of size) from the active-site cavity defined by the encapsulation of **1** by **2**. As illustrated by assembly **7**, the effective cavity size can be further manipulated by incorporating (again, by coordinative directed assembly) up to two additional "ligands". When the cavity-tuning ligands are 3,5-dinicotinic acid dineomenthyl ester, as in **7** (the alkyl groups are not shown for clarity), the reactivity of **5**, again relative to



Scheme 2. Supramolecular complex with a functionalized cavity for enhanced selectivity in catalytic epoxidation.

that of the smaller substrate **4**, is now seven times less with the supramolecular assembly than with the naked catalyst. In addition, the cavity tuning allows for significant (fourfold) differentiation of even very sterically similar substrates, such as **4** and **6**. As expected, changing the size of the cavity-tuning ligand leads to tailorable size selectivity.

Although molecular modeling suggests that **5** should be completely excluded by the modified assembly **7**, we propose that the obtained modest selective exclusion of **5** results from ligand coordination on the outside of the cavity at some of the sites. Since zinc porphyrins can accommodate only one axial substituent,[18, 19] ligation on the outside will preclude ligation on the inside of the square where it can influence the reaction selectivity. More importantly, the walls of the square are fairly free to rotate (around the Re–N bonds) in solution, thus providing a more flexible system than predicted by studies on thin films.[20–22] The preceding argument may also account for an observed lack of enantioselective reaction in cases where optically active cavity-modifying ligands were employed.

In conclusion, the formation of a supramolecular complex imparts stability and substrate selectivity to a simple manganese-porphyrin-based epoxidation catalyst. Additionally, the modular design and synthetic simplicity of the directed-assembly catalyst system is readily tunable and easily modified. The metalloporphyrin catalyst **1** resembles, both structurally and functionally, the catalytic core of cytochrome P450. The encapsulating framework, on the other hand, strongly resembles functionally, if not structurally, the stability- and selectivity-inducing protein superstructure of cytochrome P450 and other enzymes (Figure 1). With appropriate cavity functionalization, the catalyst design concept should enable partial or complete substrate exclusion or inclusion based on other physical or chemical characteristics of the substrate.

Experimental Section

Typical epoxidation procedure: The manganese catalyst **1** or **3** (3 μmol) and molecular square **2** (3 μmol) were combined in dichloromethane (3 mL). Styrene (500 equiv) and octane (14.6 μL, internal GC standard) were added to this solution. Solid iodosylbenzene (100 equiv) was then added every 10 min for 200 min. Additional styrene (500 equiv) was added at 30 min intervals. For studies at high dilution, the manganese catalyst **1** or **3** (3×10^{-9} mol) and molecular square **2** (3 μmol) were combined in dichloromethane (3 mL). Styrene (500000 equiv) and octane (14.6 μL) were added to this solution. PhIO (100000 equiv) was then added in one portion.

Samples (50 μL) were taken periodically and filtered through a silica plug to remove the catalyst. The plug was washed with dichloromethane (3 × 0.5 mL). The filtrates were combined and analyzed by quantitative GLC analysis (HP-5 column, 5° min^{-1} temperature increase, 50 °C initial oven temp, 100 °C final temp). The total turnover number was determined as the total concentration of oxidation products (styrene oxide (ca. 92 %) and phenylacetaldehyde (ca. 8 %)) divided by the initial catalyst concentration.

The epoxidation selectivity experiments were conducted as follows: MnDPyP (3 μmol, 1 equiv) and [Re(ZnDPyP)]$_4$ (1 equiv) were dissolved in dichloromethane (3 mL) followed by the addition of modifying ligands (30 – 300 equiv). *cis*-Stilbene (100 equiv) and **5** or **6** (100 equiv) were added to the mixture. PhIO (100 equiv) was then added. Samples (250 μL) were taken after 10, 20, and 30 min, passed through a neutral alumina plug with pentane eluent (15 mL), and analyzed by HPLC (nitrile column eluted with hexanes). Selectivity is defined as [*cis*-stilbene oxide+*trans*-stilbene oxide]/[sum of epoxides from **5** or **6**] and normalized against MnDPyP.

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[15] Control experiments using *fac*-[Re(CO)$_3$(pyridine)$_2$Cl] (a surrogate for the corner structures of the square, **2**), ZnDPyP, or H$_2$DPyP with styrene and iodosylbenzene gave no detectable epoxidation products.

[16] The rate of catalysis with the supramolecular assembly, however, was a factor of three slower than for the naked catalyst. Electronic effects are unlikely to account for the difference, since the strength of the coordination bonds linking **1** to **2** are comparatively weak and since the pyridine groups used by the catalyst to drive directed-assembly are almost certainly oriented out-of-plane with respect to the catalyst's metalloporphyrin core. We tentatively ascribe the rate decrease instead to hindered transport of reactants into the encapsulated active site.

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A Three-Dimensional Ferrimagnet with a High Magnetic Transition Temperature (T_C) of 53 K Based on a Chiral Molecule**

Katsuya Inoue,* Hiroyuki Imai, Prasanna S. Ghalsasi, Koichi Kikuchi, Masaaki Ohba, Hisashi Ōkawa, and J. V. Yakhmi

Investigation of molecule-based magnets, which began in the late 1960s, has led to the successful synthesis of room temperature magnets.[1] Specific features considered in molecule-based magnets include: 1) the ability to design the magnet as well as its structural dimensionality, 2) magnet solubility in water or organic solvents, and, 3) the optical transparency of the magnet.[2] The physical characteristics of greatest interest are the optical properties, particularly with respect to natural optical activity. On the basis of theoretical calculations, new phenomena were expected in optically active magnetic materials.[3] In 1997, Rikken and Raupach observed a small magneto-chiral dichroism (MChD) effect in a chiral paramagnetic material.[4] This effect depends on the

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