mer), 102745-52-8; (±)-3-cyclohexen-1-ol, 72137-22-5; (±)-(*cis*)-1,3-cyclohexanediol, 103668-41-3; (±)-2-cyclohexene-1-methanol, 103668-33-3; (±)-(*cis*)-2-(hydroxymethyl)-1-cyclohexanol, 96553-66-1; (±)-(*cis*)-5-isopropenyl-2,2,4-trimethyl-1-oxa-2-silacyclopentane, 103668-51-5; (±)-2,4,4-trimethyl-5-(2-*tert*-butyldimethylsilyloxy-1-methylethyl)-1-oxa-2-silacyclopentane (stereoisomer), 103668-52-6; (±)-2,2,4-trimethyl-3-(2-benzyloxy-1-methylethyl)-1-oxa-2-silacyclopentane (isomer 1), 103668-54-8; (±)-2,2,4-trimethyl-3-(2-benzyloxy-1-methylethyl)-1-oxa-2-silacyclopentane (isomer 2), 103729-89-1.

Supplementary Material Available: Preparative methods for the starting materials, stereochemical assignments of 1,3-diols listed in Table I, and 400-MHz ^{1}H NMR spectra of acetonides of **1**–**3** and **7** (6 pages). Ordering information is given on any current masthead page.

Membrane-Bound Cytochrome P-450 Mimic. Polymerized Vesicles as Microreactors

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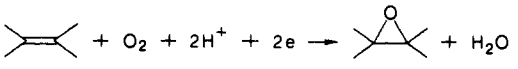
The Cytochrome P-450 dependent monooxygenases are membrane-bound enzymes that catalyze a great variety of reactions, among which is the epoxidation of alkenes by molecular oxygen.[1]



The active center of the enzymes contains an iron(III) protoporphyrin IX and axial thiolate ligand. After being reduced to iron(II) this center binds and cleaves molecular oxygen, whereupon water and a high-valent iron–oxo complex are formed. The latter species transfers its oxygen to a substrate molecule.[1,2] The electrons required in the process are provided by NADPH via a coupled electron transferring enzyme system.[1] We describe here a synthetic model system of cytochrome P-450 which incorporates all the features of the natural enzyme system, i.e., (i) a membraneously bound metalloporphyrin (complex **1**), (ii) an axial ligand (*N*-methylimidazole), (iii) an electron donor (colloidal Pt–H_2),[2a] (iv) an electron carrier (methylene blue), and (v) a membrane system (polymerized vesicles of **2**) which holds components within its bilayer or within its inner aqueous compartment (Figure 1).

[Tetrakis[4-(hexadecyloxy)phenyl]porphyrinato]manganese(III) acetate (**1**) was synthesized from the corresponding tetrakis(hydroxyphenyl) derivative and *n*-hexadecyl bromide by reaction with base in 3:1 v/v DMF–toluene. Compound **1** (2.7×10^{-5} M) and the isocyano surfactant **2**[3] (5×10^{-3} M) were cosonicated for 30 min in water at 25.0 °C. Subsequent polymerization[3] with nickel capronate (8.5×10^{-5} M) for 24 h yielded polymerized vesicles which had **1** incorporated into their bilayers. This was checked by dialysis and chromatographic procedures in combination with UV–vis. In a similar way, using an aqueous solution of K_2PtCl_4 (10^{-3} M), polymerized vesicles were prepared which, after passing over an anion-exchange resin (Dowex 1-X2, Cl^- form), contained **1** in their bilayers and Pt(II) (overall concentration 3.5×10^{-4} M) in their inner aqueous compartments. The Pt(II) ions within the vesicles were reduced to colloidal Pt by bubbling molecular hydrogen through the dispersions. Dynamic light-scattering experiments and electron micrographs revealed that the polymerized aggregates with Pt as well as those without had the same diameters, namely, 1000–3000 Å.

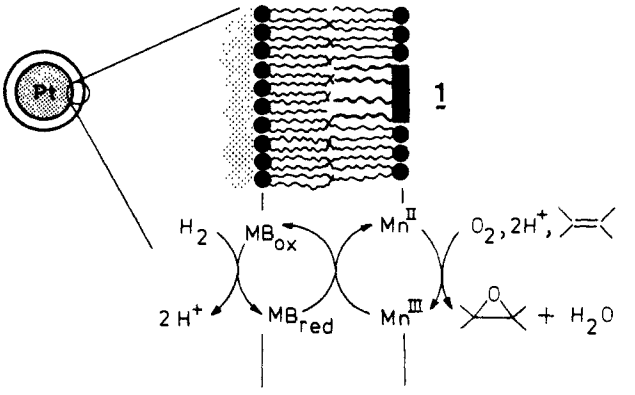


Figure 1. Polymerized vesicle as microreactor. MB_{ox} and MB_{red} stand for the oxidized and reduced forms of methylene blue, respectively.

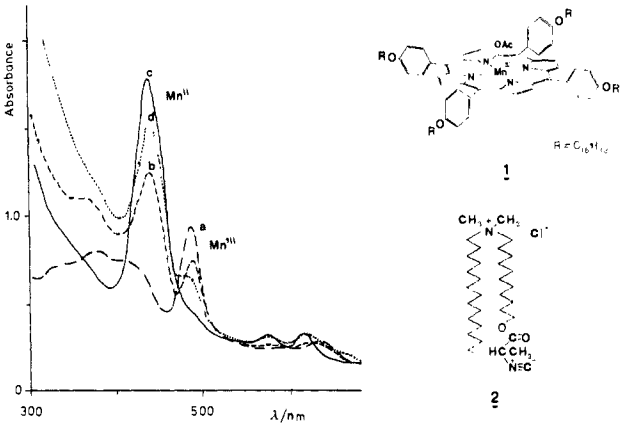


Figure 2. UV–vis spectra of manganese(III) porphyrin **1** in polymerized vesicles of **2**: (a) vesicles with or without Pt and without methylene blue after treatment with H_2; (b) same as (a) after treatment with sodium dithionite; (c) same as (b) after treatment with triton X-100; (d) vesicles with Pt and methylene blue after treatment with H_2 for 3 min.

The following experiment suggests that manganese porphyrin **1** is distributed equally between the inner and outer surfaces of the vesicles. To the polymerized vesicle dispersions (1.5 mL) containing **1**, sodium dithionite (1.5 mL, 2×10^{-3} M) was added externally. As shown by UV–vis, Mn^{III} partially reduces to Mn^{II} (50 ± 5%, Figure 2). Adding triton X-100, which causes the vesicles to leak, results in complete reduction of the manganese centers.

In order to establish the conditions under which alkenes are epoxidized by the aforementioned systems, a number of experiments had to be carried out. First, we investigated the reduction of Mn^{III} in the bilayers by molecular hydrogen. This reagent was bubbled through polymerized vesicle dispersions containing **1** and Pt in the concentrations mentioned above. Methylene blue was added in a concentration of 6.2×10^{-6} M. Blank experiments were done with vesicles without Pt and vesicles to which no methylene blue had been added. Figure 2 shows that Mn^{III} reduces to Mn^{II} when both Pt and methylene blue are present. However, when either of these components are omitted, no reduction takes place. In addition these experiments indicate that the manganese centers and Pt are located at different sites, i.e., in the vesicle bilayer and inner aqueous compartment, respectively.[4]

In a second series of experiments we tested the suitability of molecular oxygen as oxidant. Polymerized vesicles were prepared containing **1**, Pt, methylene blue, and in addition *N*-methyl-

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imidazole, which functions as an axial ligand for Mn^{III}. This system was used to catalyze the epoxidation of water-soluble (2,5-dihydrofuran, **3**) and -insoluble (styrene, **4**) alkenes.[5] The reactions followed first-order kinetics. GCMS and comparison with authentic samples showed that for **3** the reaction products are 3,4-epoxytetrahydrofuran and the ring-opened compound *trans*-3,4-dihydroxytetrahydrofuran (molar ratio 1:2.5). For **4** only the ring-opened product 1,2-dihydroxy-1-phenylethane could be detected. Turnover numbers (mol of oxygenated product/(mol of Mn^{III}·h)) for **3** and **4** amounted to 8 and 1.3, respectively. As a side reaction, the catalytic system produces water out of H_2 and O_2. The selectivity of substrate conversion vs. water formation was 2.5%. In separate experiments we checked that no oxygenation took place when any of the aforementioned components were omitted.

In summary, catalytic systems that mimic complex enzyme functions can be designed by using polymerized vesicles as microreactors.

Acknowledgment. We thank Prof. Dr. W. Drenth and A. van der Made for helpful discussion.

Registry No. 1, 103794-75-8; **2**, 103794-74-7; **3**, 1708-29-8; **4**, 100-42-5; Pt, 7440-06-4; *N*-methylimidazole, 616-47-7; methylene blue, 61-73-4; cytochrome P-450, 9035-51-2; monooxygenase, 9038-14-6.

(4) Experiments done with the water-soluble porphyrin [tetrakis(1-methylpyridinium-4-yl)porphyrinato]manganese(III) pentaiodide prove that no Pt is present in the outer aqueous compartments. Vesicles containing Pt to which this porphyrin was externally added required methylene blue to reduce Mn^{III} to Mn^{II}. Vesicles that also had K_2PtCl_4 added externally could function without the electron carrier.

(5) In a typical experiment a polymerized vesicle dispersion (2 mL, 5×10^{-3} M **2**) containing **1** (2.7×10^{-5} M), *N*-methylimidazole (5.0×10^{-4} M), methylene blue (6.2×10^{-6} M), Pt (3.5×10^{-4} M), and 2,5-dihydrofuran (4×10^{-2} M) or styrene (4.3×10^{-3} M) was stirred magnetically at 20.0 °C under an atmosphere of O_2 and H_2 (1:1 v/v). From time to time samples were taken and analyzed by GLC (Tenax-GC column). The products were identified by GCMS and by comparison with authentic samples. The pH of the reaction mixture varied between 4.5 and 5.0. In separate experiments we checked that under our conditions no H_2O_2 is produced from H_2 and O_2.

Spontaneous Assembly of Phospholipid Monolayers via Adsorption onto Gold[1]

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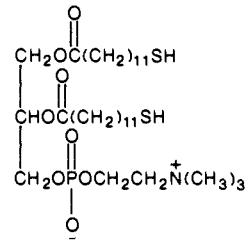
Supported phospholipid monolayers and multilayers [Langmuir–Blodgett (LB) films] represent powerful tools for probing structure–activity relationships of biomembranes.[3-5] While the preparation of such assemblies is, in theory, straightforward, monolayer transfers using film-balance techniques are nontrivial, do not always proceed with high efficiency, and are limited to planar surfaces. Moreover, the formation of supported monolayers having polar head groups extending away from the support in air is particularly difficult.[6] In this paper we describe a simple and reliable method for constructing phospholipid monolayers, based on the principle of spontaneous organization via thiol (or disulfide) adsorption onto gold surfaces.[7] Our procedure employs 1,2-bis(11-mercaptoundecanoyl)-*sn*-glycero-3-phosphocholine (**1**).[8,9]



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Resulting monolayers represent unique biomembrane models which are formed with ease and with high reproducibility and which *cannot be prepared using conventional LB methods.*

In a typical experiment, a clean glass microscope slide (75 × 25 × 1 mm) was coated with a thin layer of chromium metal (ca. 100 Å) and then coated with gold (ca. 550 Å), using a deposition rate of ca. 5 Å s^{-1}. The resulting surface was completely wetted by water (stationary contact angle was <10°), indicating the absence of contamination.[10] The slide was then immersed in 40 mL of a 4×10^{-5} M methanolic solution of **1** (chloroform or *n*-hexane can also be used) for 60 min at room temperature, removed, and rinsed by gentle agitation in an equal volume of the same solvent for 2 min. The slide was then allowed to remain in air for 0.5 h; reproducibility of lipid adsorption, as judged by ellipsometry and contact angle measurements described below, was excellent.

The advancing contact angle (θ_a) for water on this lipid-modified surface was 0°.[11] Examination of Θ_a, as a function of time of surface treatment, indicated that adsorption equilibrium was reached within 5 min. The film thickness of **1**, determined by using a Rudolph Model Auto-EL-II computerized ellipsometer (6328 Å) and assuming an index of refraction (n) of 1.52,[7] was 21.6 ± 1.9 Å (nine measurements); for $n = 1.50$, the thickness was 22.0 ± 2 Å. Space-filling models (CPK) for **1**, where the α and β chains are fully extended and perpendicular to the head group, indicate a maximum length of 24 Å. The measured thickness is, therefore, very close to that which is predicted for an assembly of **1** having *an orientation which is perpendicular*

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(2) On leave from (a) Technical University of Warsaw, Poland, and (b) A. Mickiewicz University, Poznan, Poland.

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(11) When chloroform was used as the solvent for adsorption and washing, the advancing angle was 17° after 0.5 h in air. All contact angles reported are averages of a minimum of six independent measurements on the surface and were made after 30 s of contact with water.

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