Table I. Raman Marker Bands of Cytochrome-b_5 and H39M

system	oxidtn	ν_4 (cm^{-1})	spin	coordntn	ν_3 (cm^{-1})
			5/2	6	1478–1488
heme[a]	Fe^{3+}	1368–1377	5/2	5	1491–1500
			1/2	6	1502–1507
heme[a]	Fe^{2+}	1344–1364	2	5	1471–1474
			0	6	1490–1498
Cyt-b_5	Fe^{3+}	1375	1/2	6	1510
H39M	Fe^{3+}	1373	5/2	6	1486
Cyt-B_5	Fe^{2+}	1361	0	6	1496
H39M	Fe^{2+}	1364	0	6	1497

[a] Range of values for ν_3 and ν_4 observed in heme proteins and model compounds having specified oxidation state, spin state, and coordination number.

or a water molecule is the heme axial ligand in the ferric state. The formation of the ferrous–carbon monoxide adduct is confirmed by the shift of ν_4 into the region associated with ferric species. The presence of an iron–carbon monoxide stretch at 500 cm^{-1} (data not shown) indicates that histidine rather than methionine is the axial ligand. (Sulfur ligation usually results in ~20 cm^{-1} downshift of this mode.) No stable O_2 adduct is generated; rather, in the presence of oxygen, the ferric state is immediately regenerated at room temperatures, indicating facile autoxidation of the metal center.

The effect of axial ligands on the redox potential of metal centers has been a subject of widespread interest.[9] In general, the presence of an electron rich oxygen of water (or sulfur of methionine) in the mutant cytochrome b_5 versus the histidine of the wild-type b_5 would tend to stabilize the increased positive charge of the ferric state and hence lower the observed redox potential. We found the redox potential of the H39M-b_5 protein to be −240 mV relative to the hydrogen electrode as compared to between +6 mV and −6 mV for wild-type cytochrome b_5, consistent with this interpretation.[10]

Another strong motivation for alteration of heme axial ligand environments is the possibility of generating a new protein with novel chemical properties. With an open heme cleft and possibility of ligand coordination, one might expect H39M-b_5 to have an increased peroxidase activity over the six-coordinate bis-imidazole-ligated wild-type protein. This was indeed found to be the case.[11] H39M-b_5 is also able to catalyze intermolecular oxidative chemistry as demonstrated by the hydrogen peroxide dependent oxidative demethylation of *N,N*-dimethylaniline.[12] Native cytochrome b_5 is completely inactive in this reaction, as expected for a six-coordinate electron transport protein.

In summary, we have described the first replacement of a heme protein ligand by site-directed mutagenesis. A b-type cytochrome with bis-imidazole axial ligands has been altered by replacement of one coordinating ligand to produce a hexacoordinate high-spin ferric protein. This new species has unique properties, drastically altered redox behavior, and is active in oxidative chemistry.

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(10) The redox potential of H39M-b_5 was determined by the photoreduction technique with use of EDTA as electron donor, 9-aminoacridine as photosensitizer, and Safranine T (E_o' = −289 mV) as system potential indicator as described in the following: Sligar, S.; Gunsalus, I. C. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 1079.

(11) Peroxidase activities were conducted with 1 nmol of cytochrome b_5 in 1.0 mL of 100 mM potassium phosphate buffer, pH 7.0, containing 220 nmol of hydrogen peroxide and 0.07 mg of *o*-dianisidine. An extinction coefficient of 1.13×10^4 cm^{-1} M^{-1} at 460 nm was used for product concentrations. Greater than 35 turnovers of H39M-b_5 were obtained with peroxidase activities for the various preparations of H39M-b_5, with the following activities, 4.61 U/μmol; wild-type b_5, 0.127 U/μmol protein; BSA–hemin (1:1), 0.379 U/μmol; hemin alone, 0.578 U/μmol; hemin–imidazole at ratios from 1:0.25 to 1:2, 0.729 U/μmol.

(12) Five nmol of H39M-b_5 in 0.5 mL of 100 mM potassium phosphate buffer, pH 7.0, containing 50–105 nmol of hydrogen peroxide and 500 nmoles of *N,N*-dimethylaniline as substrate, were allowed to react for 1 h at 25 °C. 1,2,4-trichlorobenzene was used as an internal standard. The reaction mixtures were extracted 3 times with chloroform and analyzed by gas chromatography on a Carbowax 20 M column with use of an HP5710A gas chromatograph and an HP3390A integrator. Reactions yielded 0.41 ± 0.03 nmol of *N*-methylaniline per nmol of hydrogen peroxide independent of the oxidant concentration corresponding to 4–8 turnovers of cytochrome.

Cooperative Binding by an Amphipathic Host

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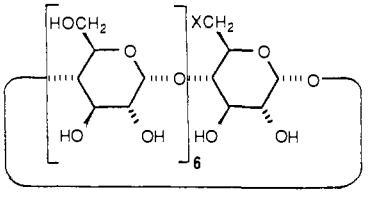
Allosteric regulation of binding and catalysis is a common feature of biochemical processes,[1] especially in the regulation of enzymes by molecular effectors. When affinity of enzyme for substrate increases with increasing effector concentration, the allostery is termed positive cooperativity, and the transition from the inactive to the active state of the protein is the allosteric transition. Allosteric transitions are typically transmitted by conformational changes,[2] though other mechanisms have also been advanced.[3] Positive cooperativity in the binding of inorganic guests to synthetic hosts has been observed in dicoronands linked by a biphenyl,[4] gable porphyrins,[5] porphyrin dimers,[6] and crystalline heme models.[7] Cooperativity has also been reported in micelle-catalyzed reactions.[8] We report here the synthesis of **4**, a new amphipathic host derived from β-cyclodextrin which exhibits positive cooperativity in the binding of simple organic guests in aqueous solution. The allosteric transition is apparently mediated by changes in aggregate morphology.



1 X = OH
2 X = OTs
3 X = $NH_3^+Cl^-$
4 X = $NH_2^+(CH_2)_{15}CH_3$ Cl^-

β-Cyclodextrin-6-monotosylate (**2**) was converted to **4** in 24% yield.[9] The association of 4-nitrophenol with **4** ([4-NP] = 0.36

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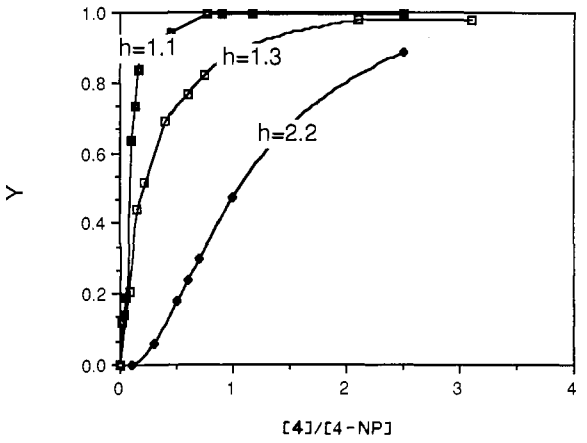

Figure 1. Binding of 4-nitrophenol to glycolipid **4**; Y = normalized change in spectroscopic observable as a fraction of the value at saturation ($\Delta\delta_i/\Delta\delta_\infty$). In DMSO (■): [4-NP] = 0.36 mM, 30 °C, Hill coefficient = 1.1 ± 0.1. Below the cmc (□): [4-NP] = 0.036 mM, [KH_2PO_4] = 1.0 mM adjusted to pH 7.00 at 29 °C, monitored at 400 nm, Hill coefficient = 1.3 ± 0.1. Above the cmc (♦): [4-NP] = 0.36 mM, [Tris-HCl] = 5.15 mM in D_2O at 30 °C, apparent pH 7.01, shift of the 4-NP protons monitored by NMR, Hill coefficient = 2.2 ± 0.1.

Table I. Association Constants and Hill Coefficients for Anionic Aromatic Guests with Cyclodextrin Hosts

host		guest[a]	K_a (M^{-1})	h	method
1		4-NP	1.2×10^3 [e]	1.0 ± 0.1	NMR, UV[c]
3		4-NP	1.0×10^3 [e]	1.1 ± 0.1	NMR
4	>cmc	4-NP	3.7×10^3 [d]	2.2 ± 0.1	NMR, UV[c]
4	>cmc	4-NBA	3.5×10^3 [d]	2.1 ± 0.1	NMR
4	>cmc	4-HBA	8.8×10^2 [d]	2.3 ± 0.1	NMR
4	>cmc	*N*-AcPhe	1.5×10^3 [d]	1.6 ± 0.2	NMR
4	>cmc	*N*-AcTrp	2.3×10^3 [d]	1.5 ± 0.2	NMR
4	<cmc	4-NP	6.2×10^4	1.3 ± 0.1	UV
4	DMSO[b]	4-NP	8.0×10^4	1.1 ± 0.1	NMR

[a] 4-NP = 4-nitrophenyl, 4-NBA = 4-nitrobenzoic acid, 4-HBA = 4-hydroxybenzoic acid, *N*-AcPhe = *N*-acetylphenylalanine, *N*-AcTrp = *N*-acetyltryptophan. [b] In DMSO-d_6. [c] Value from NMR experiment shown. [d] Estimated as $[4]^{-1}$ at $Y = 0.5$ (see Figure 1). [e] Determined by Benesi–Hildebrand analysis.[16] All experiments run at 30 °C.

mM in D_2O buffered with 5.15 mM Tris-HCl to an appparent pH of 7.01 at 30.0 °C) was probed by using ^1H NMR and UV–vis (400 nm, [**4**] = 0.068 → 0.89 mM). Instead of the hyperbolic saturation curve typical of the binding of 4-NP to β-cyclodextrin, we obtained a sigmoidal curve (see Figure 1), the hallmark of positive cooperativity.[1-4] The same behavior was observed with other guests (see Table I) and in competition experiments where [**4**] was constant while [guest] was varied. Replotting according to the Hill equation[1b,10] afforded linear graphs with slope h (= 2.2 ± 0.1 for **4** and 4-NP), the Hill coefficient,[10] which is construed as a measure of cooperativity.[1b,10] Positive cooperativity is denoted by $h > 1$. Binding of 4-NP to β-cyclodextrin (**1**) and 6-monoamino-β-cyclodextrin (**3**)[11] gave Hill coefficients of 1.0 ± 0.1 and 1.1 ± 0.1, respectively, suggesting that the alkyl substituent is necessary for cooperativity.

We surmised that the cooperativity derived from an aggregation phenomenon and determined the critical micelle concentration (cmc, conductivity measurements) of **4** in H_2O at 23 °C to be 6.5 μM and 54 μM in the presence of 40 μM 4-NP. Dynamic light scattering of **4** in H_2O revealed aggregates with an apparent hydrodynamic radius of 20 Å and a high polydispersity (>0.1). A large increase in hydrodynamic radius was observed by varying the scattering angle from 27.5 to 96.7° implying a rodlike aggregate structure.[12] The ^1H- NMR spectrum of **4** above its cmc [(**4**] = 2.79 mM in D_2O at 12 °C) showed alkyl chain resonances at δ 1.26 and 1.19 ppm.[13] Irradiation of the broader, upfield alkyl chain resonance (integration, 14 H) produced an apparent 12% NOE of all the cyclodextrin protons. Addition of 1 equiv of 4-NP reduced this to 2.7% (and *no* enhancement of the 4-NP protons) and an upfield shift of the internal cyclodextrin protons by 0.02 ppm, as in the 4-NP/β-cyclodextrin complex itself. In DMSO-d_6, only one, sharp alkyl chain resonance is observed (δ 1.22 ppm), and irradiation at this frequency effects no NOE of the cyclodextrin protons. Thus, 4-NP competes with the alkyl group for the cavity.[14] However, the cmc is *higher* in the presence of guest, even though the complex should be less soluble. Intermolecular host–guest complexation of alkyl chains by **4** would supply a driving force for aggregation even at low concentrations;[15] guests would suppress this and allow aggregation at more normal concentrations.

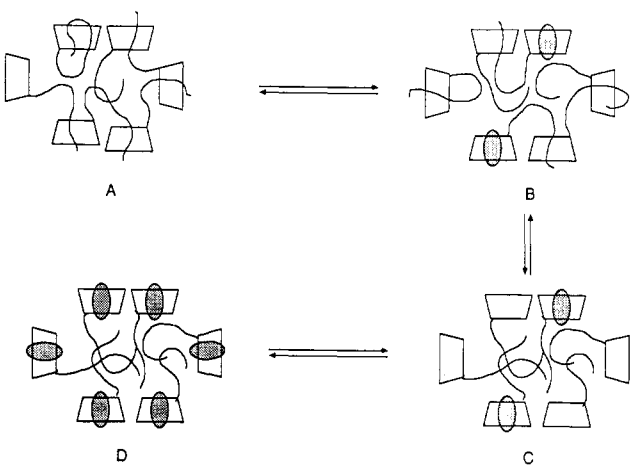

Figure 2. Schematic representation of proposed model for positive cooperativity in the binding of guests to aggregated amphipathic host **4**: (a) no guests present, alkyl chains complexed in cyclodextrin cavities; (b) introduction of guest; (c) alkyl chains partition into micelle interior; (d) vacant cyclodextrins bind more guest. For simplicity only six surfactants are shown; the actual equilibrium aggregation number is not known at this time.

The overall affinity of **4** for guests (approximated as 1/[**4**] at 50% saturation) was unremarkable above the cmc (see Table I), but, below its cmc, little or no cooperativity is observed (h = 1.3 ± 0.1), and the monomeric **4** binds 4-NP with $K_a = 6.2 \times 10^4$ M^{-1}. In DMSO-d_6 no cooperative binding is observed (h = 1.1 ± 0.1), and the 1:1 association constant is 8.0×10^4 M^{-1}. Cooperativity is also eradicated in the presence of excess SDS (71.7 mM in H_2O). Interestingly, when binding is studied such that

(9) β-Cyclodextrin-6-monotosylate (**2**) was treated with 1-hexadecylamine, KI, and DMAP in DMF at 60 °C for 24 h. After ion-exchange chromatography (Sephadex CM-25, 3:2 ethylene glycol/H_2O → 3:2 ethylene glycol/0.25 M aqueous NaCl), the hydrochloride salt **4** was isolated in 24% yield. The structure of glycolipid **4** was confirmed by ^1H NMR, ^{13}C NMR (coupled and decoupled), FT-IR, high resolution FAB-MS, and optical rotation.

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(12) It is difficult to estimate the aggregation number since the aggregate morphology is not clearly defined. The nonspherical structure is probably necessitated by the large head-group-to-tail ratio.

(13) Relative to internal $Na^+(CH_3)_3SiCD_2CD_2COO^-$. The α-, β-, γ-, and ω protons of the alkyl chain are also observed but do not change significantly under the various conditions.

(14) Intramolecular inclusion of a covalently attached lipid by cyclodextrin finds precedent in the work of Tabushi: (a) Tabushi, I.; Shimokawa, K. *J. Am. Chem. Soc.* **1980**, *102*, 5400. (b) Tabushi, I.; Kuroda, Y.; Shimokawa, K. *J. Am. Chem. Soc.* **1979**, *101*, 4759.

(15) At higher temperatures dynamic light scattering shows a slow increase in the size of the aggregates. The surfactants are apparently undergoing a slow "host–guest polymerization" via intermolecular complexation of their chains. We obtain an insoluble, fibrous, white solid which can be partially resolubilized by sonication in DMSO or repeated lyophilizations. Kamitori et al. have made cyclodextrins which exhibit intermolecular complexation: Kamitori, S.; Hirotsu, K.; Higuchi, T.; Fujita, K.; Yamamura, H.; Imoto, T.; Tabushi, I. *J. Chem. Soc., Perkin Trans. 2*, **1987**, 7.

the varying concentration of **4** crosses its cmc, the Benesi-Hildebrand[16] graph shows a clear break at the cmc. The monomeric complexation constants for **4** are extraordinarily high; there is precedent for electrostatic enhancement of binding to cyclodextrins,[17] especially in DMSO,[18] and neutral guests fail to bind to **4**. However, **3** exhibits only a modest affinity for anionic guests in water. The alkyl chain of **4** may create a more hydrophobic microenvironment[19] for the guests, thus augmenting the hydrophobic binding and magnifying the electrostatic attraction between host and guest.

A provisional model to account for positive cooperativity is depicted schematically in Figure 2. Guest binds to the cyclodextrin cavity and expels the resident alkyl chain into the micelle interior. This renders the micelle more lipophilic, causing other alkyl chains to partition out of cyclodextrin. As a result, affinity of cyclodextrin for guest is enhanced since the alkyl chains compete less effectively for the same sites. Clearly it is the aggregate that is the allosteric entity rather than any single host. We are currently investigating the generality of this novel mechanism for cooperative binding.

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Ring Size and Strain as a Control of Reaction Selectivity: Ethylene Sulfide on Mo(110)

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The adsorption and reaction of sulfur-containing organic molecules on single-crystal transition-metal surfaces form a subject of current interest to us[1] and others.[2] The primary focus of our work is an investigation of how thermodynamic properties of adsorbate molecules affect the mechanism(s) by which they react. To this end, we have studied the reactions of two saturated cyclic sulfides—trimethylene sulfide (c-C_3H_6S) and tetrahydrothiophene (c-C_4H_8S)—on Mo(110).[1a-c] On the basis of these studies we proposed that ring strain in the cyclic sulfide controls reaction selectivity on Mo(110). This work concerns the reactions of a third cyclic sulfide, ethylene sulfide (c-C_2H_4S), on Mo(110). The results presented here demonstrate that ring size as well as ring strain determines the reaction selectivity of cyclic sulfides on Mo(110).

Salient features of the reactions of tetrahydrothiophene and trimethylene sulfide on Mo(110) are summarized as follows. Certain features of their temperature-programmed reactions are similar. Each undergoes ring opening to form a thiolate intermediate which then decomposes to surface sulfur and gaseous alkanes and alkenes between 300 and 375 K. Accompanying these similarities, however, are marked differences. Some trimethylene sulfide reacts by intramolecular elimination to form cyclopropane at 190 K. No cyclobutane formation pathway is observed for tetrahydrothiophene. Tetrahydrothiophene desorbs intact from Mo(110) at 310 K, but no reversibly chemisorbed state is detected for trimethylene sulfide. These differences were rationalized by proposing that thiolate formation and intramolecular elimination are kinetically driven by loss of ring strain in the cyclic sulfide. Hence, both processes are more favorable for trimethylene sulfide (ring strain = 19 kcal/mol[3]) than for tetrahydrothiophene (ring strain = 2 kcal/mol[3]). Chemisorbed trimethylene sulfide does not desorb, because it reacts to form cyclopropane and chemisorbed propyl thiolate at a surface temperature lower than that necessary to overcome the barrier to desorption. Similarly, tetrahydrothiophene does not undergo intramolecular elimination because the transition states leading to desorption and the thiolate intermediate are more accessible than that leading to cyclobutane formation.

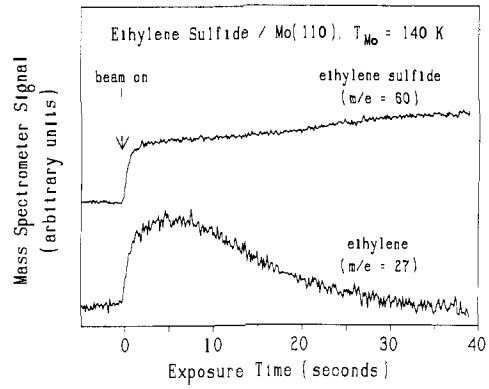

Figure 1. The mass spectrometrically determined partial pressures of ethylene and ethylene sulfide measured as a function of ethylene sulfide exposure to a Mo(110) surface held at 140 K. Ethylene sulfide impinged upon Mo(110) from an effusive source located approximately 0.5 in. from the crystal, the configuration resulting in optimal detection of ethylene. The ions detected—m/e = 27 for ethylene and m/e = 60 for ethylene sulfide—were chosen for their optimal signal-to-noise ratios. The ethylene pressure curve has been corrected by subtracting the contribution of ethylene sulfide (approximately 50% of the total signal), which also cracks at m/e = 27. During the dose the ionization gauge measured pressure rise in the chamber was approximately 1×10^{-10} Torr.

Ethylene sulfide is nearly as strained as trimethylene sulfide (18 versus 19 kcal/mol[3]). Also, ethylene formation upon adsorption of ethylene sulfide on room temperature Cu(110) has been previously inferred.[4] We therefore expected that intramolecular elimination of ethylene from ethylene sulfide would be as favorable as intramolecular elimination of cyclopropane from trimethylene sulfide. We find that intramolecular elimination is the dominant observed reaction pathway, occurring upon adsorption for crystal temperatures as low as 100 K, with an activation energy of $\leq$6 kcal/mol.[5] In contrast to trimethylene sulfide, no competitive ring opening to a thiolate occurs, a fact which does not reflect any inherent instability of the C_2 thiolate.[6] Furthermore, as opposed to other cyclic sulfides, complete decomposition of ethylene sulfide to surface carbon and sulfur is a minor reaction pathway, accounting for approximately 15% of all irreversibly chemisorbed ethylene sulfide.

Exposure of a cold Mo(110) surface to an effusive source of room temperature ethylene sulfide[7] results in the immediate ev-

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