electron transfer is at least 20 kcal/mol endothermic, the toluene radical anion being unbound in the gas phase. For most of the benzylic systems we have examined, the ET step is endothermic, although the energy released in forming the collision complex may still allow it to occur. It is possible that the direct proton transfer and the ET/HAT paths would have different isotope effects,[21] but low-pressure gas-phase ion-molecule experiments have usually been unable to reveal such details because of the chemical activation aspects of the dynamics.[22]

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(21) Wellman, K. M., Victoriano, M. E.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 2242. Noest, A. J.; Nibbering, N. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 383. These authors have been able to measure small kinetic isotope effects for bimolecular reactions.

(22) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906. This paper contains a discussion of some of the difficulties in interpreting kinetic isotope effects for these kinds of reactions.

Cyclodextrin Sandwiched Fe_4S_4 Cluster

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Since Holm and co-workers first reported the synthetic Fe_4S_4 type cluster mimicking the active site core of ferredoxin, the chemical and physical properties of these synthetic clusters have been extensively investigated.[1] These synthetic clusters, however, are usually unstable in an *aqueous* solution because of their facile hydrolytic degradations,[2] quite contrary to the natural ferredoxins.[3] Therefore, their redox reactivities in aqueous solution have been investigated only under the limited conditions where micelles,[4] bilayer membranes,[5] or high concentration of mercaptans[2,6] were used as the stabilizing cofactor. In the present paper, we wish to report the synthesis and redox reactivities of a new type of the synthetic clusters, **2** and **3**, which are stable in an aqueous solution without any additional stabilizing reagents and have the hydrophobic recognition site of cyclodextrin.[7]

6A,6D-Biphenyl-4,4′-disulfonyl-capped β-cyclodextrin was converted to the target cluster **2** via dimercaptan **1** by the ligand exchange reaction[8] under the conditions listed in Chart I.[9] The product (114 mg, 83% yield) was analyzed as a tetrahydrate.[10]

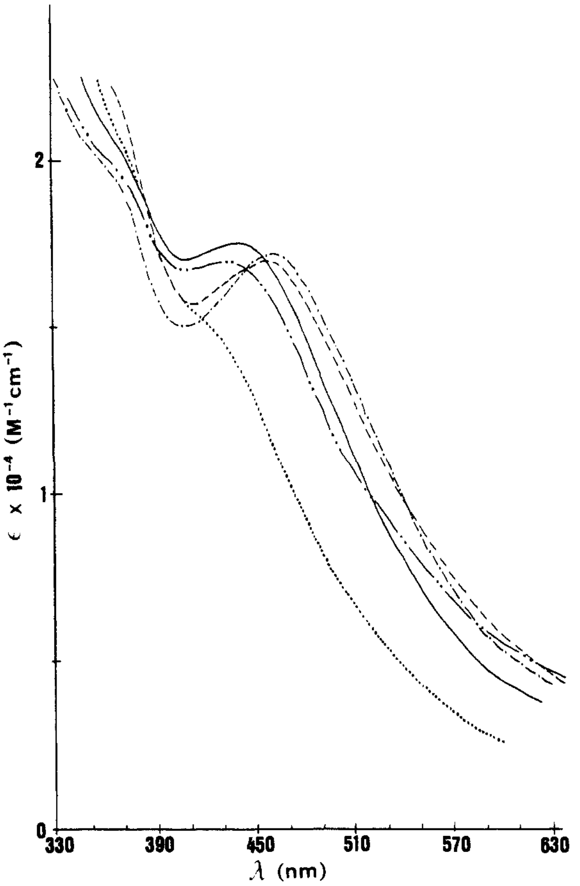
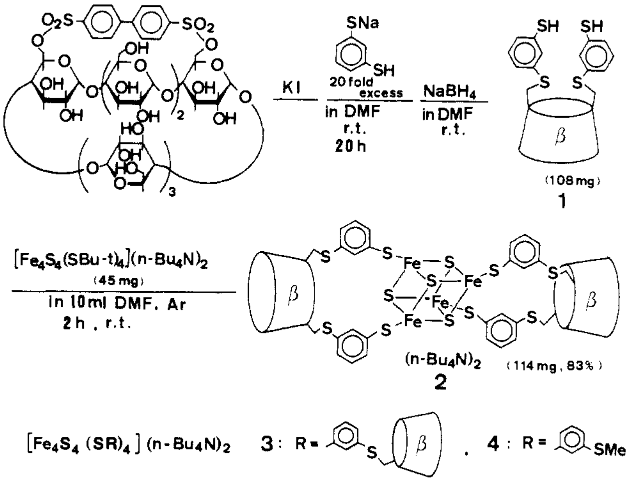


Figure 1. Electronic spectra of **2** (—), **3** (– – –), **4** (–·–) in DMF solution, **2** (—··—) in the 10 mM phosphate buffer (pH 7.0) (cell length = 1 cm), and **2** (···) electrolyzed at −1.15 V versus Ag/AgCl electrode in the DMF solution containing 0.1 M *n*-Bu_4NBr supporting electrolyte at 25 °C under Ar (cell length = 0.05 cm, see ref 11).

Chart I



The reference compounds **3** and **4** were also prepared by the similar ligand exchange reaction.

Physical properties of **2**, **3**, and **4** are summarized in Table I and Figure 1. As shown in Figure 1, the electronic spectra of **2**, **3**, and **4** exhibit the typical absorption bands of the Fe_4S_4 cluster (λ_{max} (nm) (ϵ) (DMF) **2**: 369 (sh, 20 700), 441 (17 500); **3**: 374 (sh, 20 300), 458 (17 000); **4**: 364 (sh, 19 600), 463 (17 300)). The reduction potentials of **2**, **3**, and **4** in DMF measured by a cyclic voltammetry were −0.94, −0.93, and −0.92 V versus Ag/AgCl at 25 °C, respectively. The reduced form of **2**, which was easily generated by using the thin-layer spectroelectrochemical cell reported by Saveant et al.,[11] reproduced the oxidized form

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[†] Deceased on March 22, 1987.

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(6) Hill, C. L.; Renaud, J.; Holm, R. H.; Mortenson, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 2549.

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(10) Found (calcd for $C_{140}H_{224}N_2O_{66}S_{12}Fe_4{\cdot}4H_2O$) C: 45.63 (45.80), H: 6.56 (6.37), N: 0.72 (0.76), Fe: 5.8 (6.08). The molecular weight measured by the light scattering method is $(3.7 \pm 0.2) \times 10^3$ (calcd 3671.35). For the light scattering method, see: Huglin, M. B. *Light Scattering from Polymer Solutions*; Academic Press: New York, 1972.

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Table I. Physical Properties of Fe_4S_4 Clusters at 25 °C under Ar (λ_{max} (ϵ), half-life,[a] and $E^{1/2}$ (versus Ag/AgCl))

	$Fe_4S_4((SPh\text{-}m\text{-}S)_2CD)_2$ (**2**)	$Fe_4S_4(SPh\text{-}m\text{-}SCD)_4$ (**3**)	$Fe_4S_4(SPh\text{-}m\text{-}SMe)_4$ (**4**)
in H_2O (10 mM phosphate buffer, pH 7.0)	428 nm (17 000) 120 h –0.58 V	468 nm (17 000) 70 h –0.55 V	468 nm[b] 5.6 h[b] –0.54 V[b]
in DMF	441 nm (17 500) *c* –0.94 V[d]	458 nm (17 000) *c* –0.93 V[d]	463 nm (17 300) *c* –0.92 V[d]

[a] By monitoring the decreases of the characteristic absorptions of clusters at 420–470 nm. [b] 5% DMF–95% 10 mM phosphate buffer, pH 7.0. [c] No appreciable spectral changes were observed for several days. [d] 100 mM n-Bu_4NBr.

by applying –0.50 V versus Ag/AgCl of the anodic potential in over 95% yield based on the spectral absorbance (see Figure 1).

The present synthetic clusters **2** and **3** are soluble in water[12] without any solubilizing reagents, and a small amount of **4** (ca. 0.1 mM) is also able to be solubilized in 5% DMF–H_2O. The reduction potentials of **2**, **3**, and **4** in aqueous solution at pH 7.0 were observed to be –0.58, –0.55, and –0.54 V versus Ag/AgCl, respectively. Observed positive shifts of reduction potentials by the solvent change ($E^{1/2}_{H_2O} - E^{1/2}_{DMF}$ = 0.36–0.38 V) lie within the range of those reported for other synthetic clusters.[6]

The most remarkable characteristics of **2** and **3** are their stabilities in aqueous solution. The half-lives at pH 7.0 (25 °C) of **2** and **3** in the aqueous phosphate buffer, without any additional thiols, are greater than 120 and 70 h, respectively, based on absorbance changes of the electronic spectra of **2** and **3**, while that of the reference cluster **4** is only 5.6 h in 5% DMF–H_2O. Thus, **2** and **3** are 21- and 13-fold more stable than **4** in aqueous solution, respectively, though the stability of **4** is higher than that expected from the data reported for other clusters having alkylthiolate ligands.[13] Since consideration of CPK space filling molecular models of **2** and **3** shows that the primary OH groups of cyclodextrin can attack iron atoms of the cluster core *intramolecularly*, present enhanced stabilities of **2** and **3** may be attributed to the favorable shift of ligand exchange equilibrium toward the cluster formation by the competition of water with these primary OH groups of cyclodextrin.[2]

Finally, it should be noted that the λ_{max}'s of the electronic spectra of **3** and **4** show a small red shift when the solvent is changed from DMF to H_2O rather than the blue shift usually reported for alkylthiolate clusters, while **2** shows the normal blue shift.[6] Although at the present stage it is not clear whether the observed red shift is the general trend for arenethiolate clusters or not, there is a possibility that a mechanism other than the solvation on sulfur atoms,[6] such as steric effects,[14] is operating for the absorption shift by solvent change in the present case.

The present new iron–sulfur clusters have great advantage in that the hydrophobic pockets of cyclodextrins may be available as recognition sites for substrates such as an electron donors and/or acceptors. Applications of these water soluble clusters, especially focusing on **2**, are now in progress in our laboratory.

Acknowledgment. We thank Toshio Tanaka and Koji Tanaka, Osaka University, for their kind advice on the electrochemical experiments for the present compounds.

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(11) Lexa, D.; Saveant, J. M.; Zickler, J. *J. Am. Chem. Soc.* **1977**, *99*, 2786.

(12) The solubility of **2** in the 10 mM phosphate buffer (pH 7.0) is ca. 11 mg/mL (3.0 mM).

(13) Although there are no available data treating the stabilities of arenthiolate Fe_4S_4 clusters in aqueous solution, during the investigation of this paper, one of referees suggested that arenthiolate Fe_4S_4 cluster was expected to be more stable than the alkylthiolate one due to the weaker proton acceptance ability of arenethiolates.

(14) Ueyama, N.; Sugawara, T.; Fuji, M.; Nakamura, A.; Yasuoka, N. *Chem. Lett.* **1985**, 175.

Absolute Rates of Dimerization and Cycloaddition of 3,4-Dimethylenefuran and 3,4-Dimethylenethiophene by Nanosecond Time-Resolved Spectroscopy[1a]

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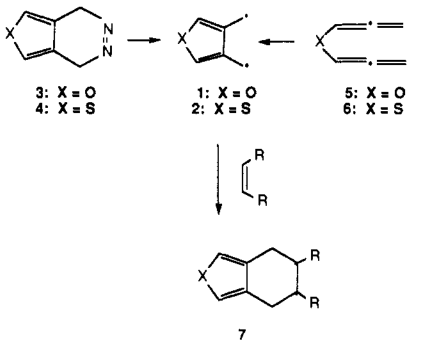
3,4-Dimethylenefuran (**1**) and 3,4-dimethylenethiophene (**2**) can be generated in fluid solutions from the corresponding diazenes, **3** and **4**,[3-5] and from the corresponding bis-allenes, **5** and **6**.[6-8] The capture of the singlet[3-5,9] biradicals **1** and **2** by alkenes to give cycloadducts (**7**) is believed to involve the same intensely colored species (**1**, λ_{max} = 560 nm; **2**, λ_{max} = 572 nm) observed spectroscopically from **3** and **4** immobilized in low-temperature glasses or flash photolyzed in solution, although heretofore no direct evidence on this point has been available.

We now report direct time-resolved spectroscopic observations of the kinetic behavior of these transients generated from diazenes **3** and **4** by nanosecond flash photolysis.[10] Deoxygenated samples of **3** or **4** in either CH_3CN or toluene solution in a 3 × 7 mm static cell (initial optical densities about 0.4 at 337 nm) were kept at 260–263 K to minimize thermal decomposition and subjected to 337-nm laser pulses. Transient spectra with maxima at about 560 (**1**) and 572 (**2**) nm were observed with an optical multichannel analyzer. Typically, the pulses produced initial transient concentrations of (1–2) × 10^{-5} M. The decay of the transient absorption with time was monitored by a photomultiplier-transient digitizer system.



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(1) (a) Issued as NRCC 28742. (b) National Research Council of Canada.

(2) Yale University.

(3) Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088.

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(5) Zilm, K. W.; Merrill, R. A.; Webb, G. G.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.*, submitted for publication.

(6) (a) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *Tetrahedron Lett.* **1987**, *28*, 4263. (b) A referee has asked whether it is possible that the purple compound is in rapid equilibrium with another species which actually undergoes the cycloaddition. In the absence of a specific proposal as to what the second species might be, it is difficult to give a definitive answer, but the two most likely candidates are the [3,4]cyclobuta heterocycle and the 2,3-dimethylene-5-oxa(or thia)bicyclo[2.1.0]pentane. The cyclobutanes are stable under the reaction conditions, and neither of the bicyclopentanes would be expected to react in preference to the purple biradical and at an absolute rate near the encounter-controlled frequency.

(7) Braverman, S.; Duar, U.; Segev, D. *Tetrahedron Lett.* **1976**, 3181.

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(10) The nanosecond laser system has been described elsewhere: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.