

Electron Transfer Reaction between  $\text{Fe}_4\text{S}_4$  Cluster and Methyl Viologen

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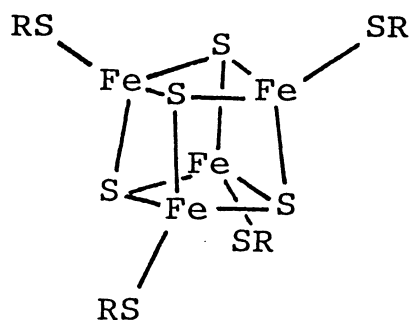
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The reduction of  $\text{Fe}_4\text{S}_4^{2+}$  to  $\text{Fe}_4\text{S}_4^{1+}$  with the reduced form of methyl viologen, was found to proceed with the synthetic clusters ligated with pentafluorobenzenethiolate.

$\text{Fe}_4\text{S}_4$  clusters have been found widely in a variety of functional proteins, including physiologically important electron carriers, ferredoxins, and several enzymes, such as hydrogenase, CO-dehydrogenase, sulfite reductase. The redox property of  $\text{Fe}_4\text{S}_4$  cluster plays the key role for the functions of these proteins. The synthetic clusters,<sup>1,2)</sup>  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$  have served as accurate models of these sites, and their physicochemical properties have been characterized extensively. However, the electron transfer reactions using these synthetic clusters have been scarcely attempted so far except for the self exchange reactions.<sup>3)</sup> This is mainly because of the low reduction potentials of these synthetic clusters ( $< -1.0$  V). Since the conventional electron donors, methyl viologen and bipyridines possess the higher potentials, the reduction of the clusters with these electron donors can not be achieved. In this letter we hope to describe the electron transfer reaction using  $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{F}_5)_4]^{2-}$ ,  $1^{2-}$ , which has a relatively high reduction potential.

All procedures were performed under an argon atmosphere. The solvents were carefully purified before use by conventional methods.  $1^{2-}$  was prepared by the ligand substitution reaction from  $[\text{Et}_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SBU}^t)_4]$  and pentafluorobenzenethiol.<sup>4)</sup>  $1^{3-}$  was isolated by the reduction of  $1^{2-}$  by sodium acenaphthyle-

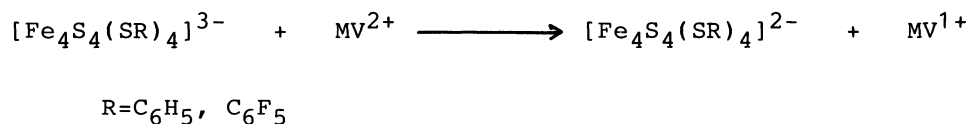


- |   |                        |
|---|------------------------|
|   | R                      |
| 1 | $\text{C}_6\text{F}_5$ |
| 2 | $\text{C}_6\text{H}_5$ |

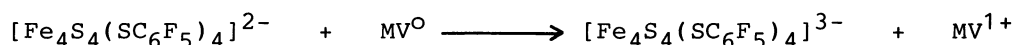
nide in HMPA.<sup>5,6)</sup>  $1^{2-}$  exhibits the characteristic weak shoulder bands at ca. 410 nm (ascribed to S-Fe charge transfer) and at ca. 340 nm, while  $1^{3-}$  shows a band at 345 nm.

The cyclic voltammogram<sup>7)</sup> of  $1^{2-}$  (tetraethylammonium perchlorate as supporting electrolyte, in acetonitrile) consists of the reversible couple at  $E_{1/2}$ , -0.75 V vs. SCE which is ascribed to  $1^{2-}/3^{-}$ . The couple corresponding to  $1^{3-}/4^{-}$  is observed as an irreversible wave at ca. -1.2 V. The reduction potential of  $1^{2-}$  is thus considerably higher than the values of the conventionally known synthetic  $Fe_4S_4$  clusters, and even several artificial electron donor reagents.

Methyl viologen (MV) in its reduced forms is used for a variety of enzymic reactions in vitro as electron donor. It has two reversible couples at -0.69 V ( $MV^{2+}/MV^{1+}$ ) and -1.02 V ( $MV^{1+}/MV^0$ ).<sup>9)</sup> First attempted was the stoichiometric reduction of  $MV^{2+}$  to  $MV^{1+}$  using  $1^{3-}$  and  $2^{3-}$ . As expected from the low reduction potential,  $2^{3-}$  reduces  $MV^{2+}$  to  $MV^{1+}$  in DMF; the appearance of new bands at 395 and 605 nm due to  $MV^{1+}$  as well as at 460 nm due to  $2^{2-}$  evidently confirms to the complete reduction of  $MV^{2+}$  with an equimolar amount of  $2^{3-}$ . Since the reaction is so fast, we could not observe the development of the new absorption bands in this case. On the other hand, the reaction of  $MV^{2+}$  and  $1^{3-}$  undergoes very slowly, and it is possible to follow the time course of the reaction spectroscopically.



The reduction of  $1^{2-}$  with  $MV^0$  was attempted. In these experiments,  $MV^0$  was prepared by the reduction with sodium amalgam in THF and added into the solution of  $1^{2-}$  in DMF under purified argon. The electronic spectrum of the resulting solution was shown in Fig. 1. The characteristic absorption bands for  $MV^{1+}$  appeared at 395 and 605 nm. No band due to  $1^{2-}$  at 410 nm is observed besides the appearance of the new band at 345 nm. Hence, the following reduction proceeds evidently. Although the same reaction was also attempted with  $2^{2-}$ , no reduction of  $2^{2-}$  was detectable.



2,2'-Dimethyl bipyridine with the reduction potential at -0.96 V has been found to be effective as electron donor for hydrogen evolution catalyzed by hydrogenase.<sup>10)</sup>  $1^{2-}$  was reduced with the reduced form of 2,2'-dimethyl bipyridine as well. As summarized in Table 1, the reaction directions of the electron transfer reactions can be anticipated based on their reduction potentials.

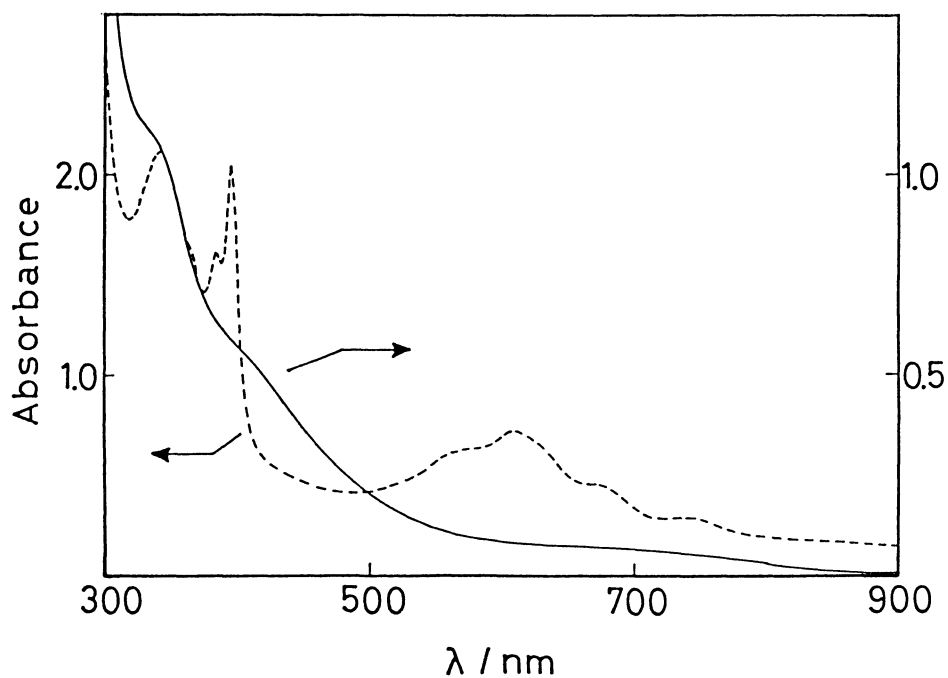


Fig. 1. Electronic spectra of  $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{F}_5)_4]^{2-}$  and the resulting solution of  $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{F}_5)_4]^{2-}$  reacted with  $\text{MV}^0$  in acetonitrile.

:  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SC}_6\text{F}_5)_4]$  ( $5.92 \times 10^{-5} \text{ mol dm}^{-3}$ )

: the same volume of the solutions,  $\text{MV}^0$  ( $1.18 \times 10^{-4} \text{ mol dm}^{-3}$ ) and  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SC}_6\text{F}_5)_4]$  ( $1.18 \times 10^{-4} \text{ mol dm}^{-3}$ ), were mixed.

Table 1. Electron transfer reactions between  $\text{Fe}_4\text{S}_4$  clusters and bipyridinium salts

Reaction	R= $\text{C}_6\text{H}_5$	R= $\text{C}_6\text{F}_5$
$\text{t}^{3-} + \text{MV}^{2+} \longrightarrow \text{t}^{2-} + \text{MV}^{1+}$	r.p.	r.p.
$\text{t}^{2-} + \text{MV}^0 \longrightarrow \text{t}^{3-} + \text{MV}^{1+}$	n.r.	r.p.
$\text{t}^{2-} + \text{bipy}^{1+} \longrightarrow \text{t}^{3-} + \text{bipy}^{2+}$	-	r.p.

$\text{t}^{2-} = [\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ , MV = methyl viologen, bipy = 2,2'-dimethyl bipyridine

r.p. denotes the reaction proceeded.

n.r. denotes the reaction did not proceed.

$E_{1/2}$  vs. SCE:  $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]^{2-/3-}$ , -1.04;  $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{F}_5)_4]^{2-/3-}$ , -0.75;

$\text{MV}^{2+/1+}$ , -0.69;  $\text{MV}^{1+/0}$ , -1.02;  $\text{bipy}^{2+/1+}$ , -0.96 V

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- 4) Satisfactory elemental analysis was obtained.  $^{19}\text{F}$ -NMR ( $\delta$ ,  $\text{d}_6$ -MeCN,  $\text{CF}_3\text{COOH}$ ), -33.7 (s, 2F, o-Ph), -81.4 (s, 1F, p-Ph), -86.6 ppm (s, 2F, m-Ph); electronic spectrum in DMF, 410 nm ( $\epsilon$ ,  $8700 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ), 340 nm (18000).
- 5) Satisfactory elemental analysis was obtained. Electronic spectrum in DMF, 345 nm (17000).
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