A 4Fe–4S Cluster with 1-Adamantanethiolate Ligand as a Synthetic Analogue of High Potential Iron–Sulphur Proteins

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A 4Fe–4S cluster with the 1-adamantanethiolate (SAd) ligand, $(Et_4N)_2[Fe_4S_4(SAd)_4]$, has been prepared as the first synthetic analogue of high potential iron-sulphur proteins (HiPIP), and shows the $[Fe_4S_4]^{2+/3+}$ redox couple both in dimethylformamide and in aqueous solution.

4-Fe Ferredoxins mediate electron transfer between $[Fe_4S_4]^{+/2+}$ redox couples, while those mediated by high potential iron–sulphur proteins (HiPIP) are related to $[Fe_4S_4]^{2+/3+}$ redox couples.[1] Thus, iron–sulphur proteins containing Fe_4S_4 cores can adopt three different oxidation levels, $[Fe_4S_4]^{n+}$ (n = 1,2,3). In $Bu^n_4NBF_4$·3toluene $[Fe_4S_4(SPh)_4]^{2-}$ exhibits the reversible $[Fe_4S_4]^{0/+,+/2+,2+/3+}$ redox couples,[2] but synthetic 4Fe–4S clusters usually show only the reversible or quasi-reversible $[Fe_4S_4]^{+/2+}$ redox couple in ordinary solvents.[3] On the other hand, 4Fe–4S clusters with bulky ligands such as 2,4,6-tri-isopropylbenzenethiolate,[4] tripeptide,[4] and 36-membered macrocyclic thiolates[5] provide the quasi-reversible or reversible $[Fe_4S_4]^{2+/3+}$ redox couple in dry organic solvents. As an analogue of HiPIP, the redox behaviour of the $[Fe_4S_4]^{2+/3+}$ couple in aqueous solution is also of interest. We, therefore, have prepared $(Et_4N)_2[Fe_4S_4(SAd)_4]$† with 1-adamantanethiolate (SAd) as a bulky ligand with the intention of stabilizing both the $[Fe_4S_4]^{+/2+}$ and $[Fe_4S_4]^{2+/3+}$ redox couples not only in an organic solvent but also in aqueous poly[2-(dimethylamino)-hexanamide] (PDACA)‡ solution.

The cyclic voltammogram of $(Et_4N)_2[Fe_4S_4(SAd)_4]$ in dimethylformamide (DMF) shows the reversible $[Fe_4S_4]^{+/2+}$ and $[Fe_4S_4]^{2+/3+}$ redox couples at $E_{1/2}$ −1.32 V *vs.* s.c.e.§ (E_{pc} −1.36 and E_{pa} −1.28 V) and −0.10 V *vs.* s.c.e. (E_{pc} −0.14 and E_{pa} −0.06 V), respectively, as shown in Figure 1. An aqueous PDACA solution (pH 7.3) of $(Et_4N)_2[Fe_4S_4(SAd)_4]$ also clearly displayed the $[Fe_4S_4]^{+/2+}$ and $[Fe_4S_4]^{2+/3+}$ couples at $E_{1/2}$ −0.90 and −0.28 V *vs.* s.c.e., respectively, when an ITO (indium–tin oxide) electrode¶ was used as a working electrode. In contrast to the DMF solution, both redox processes are quasi-reversible in an aqueous medium, since the peak separations between anodic and cathodic peaks of those couples are 170 mV. The $E_{1/2}$ value of the $[Fe_4S_4]^{+/2+}$ couple in water was shifted anodically by 420 mV compared with that in DMF, similarly to clusters such as $[Fe_4S_4(SC_6H_4\text{-}p\text{-}C_8C_{17}{}^n)_4]^{2-}$ in aqueous PDACA solution,[7] whereas the oxidation of $[Fe_4S_4(SAd)_4]^{2-}$ in an aqueous PDACA solution takes place more cathodically by 180 mV than that in DMF.

Figure 2 shows the electronic absorption spectra of $[Fe_4S_4(SAd)_4]^{2-}$ in DMF and in aqueous PDACA solutions at pH 7.3 and 5.6, respectively. The absorption maxima at $\lambda_{max.}$ 415 and 315 nm in DMF (Figure 2a) are close to those of $[Fe_4S_4(S\text{-}2,4,6\text{-}Pr^i_3C_6H_2)_4]^{2-}$.[4] The electrochemical reduction of $[Fe_4S_4(SAd)_4]^{2-}$ at −1.60 V *vs.* s.c.e. in DMF caused the shift of the two ligand to metal charge transfer (LMCT) bands to 365 and 290 nm, respectively. On the other hand, two

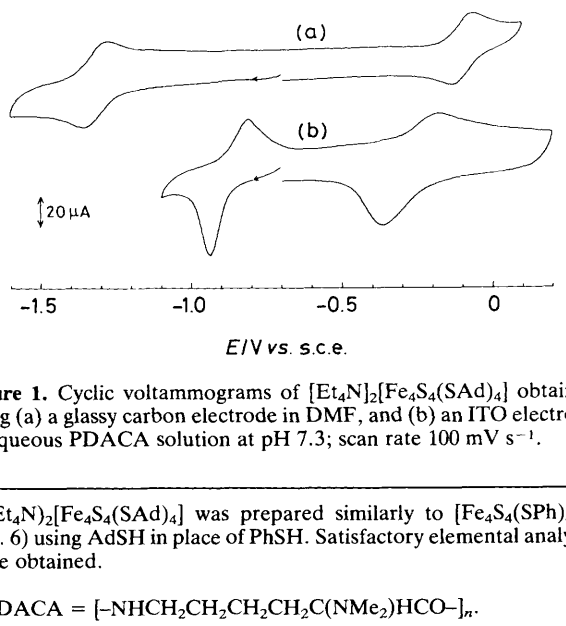

Figure 1. Cyclic voltammograms of $[Et_4N]_2[Fe_4S_4(SAd)_4]$ obtained using (a) a glassy carbon electrode in DMF, and (b) an ITO electrode in aqueous PDACA solution at pH 7.3; scan rate 100 mV s^{-1}.

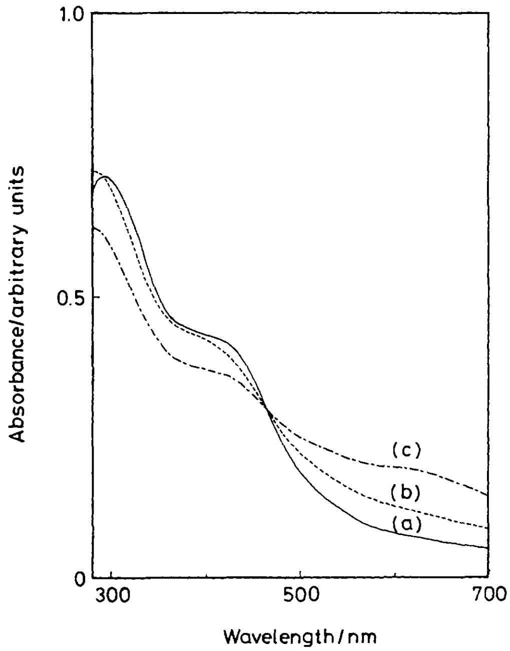

Figure 2. Electronic absorption spectra of $[Et_4N]_2[Fe_4S_4(SAd)_4]$ (3.2×10^{-4} M) (a) in DMF (——) and in aqueous PDACA solutions at (b) pH 7.3 (----) and (c) pH 5.6 (—·—).

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† $(Et_4N)_2[Fe_4S_4(SAd)_4]$ was prepared similarly to $[Fe_4S_4(SPh)_4]^{2-}$ (ref. 6) using AdSH in place of PhSH. Satisfactory elemental analyses were obtained.

‡ PDACA = $[\text{–NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C(NMe}_2\text{)HCO–}]_n$.

§ The $E_{1/2}$ value was estimated as the average of the E_{red} and E_{ox} values.

¶ The $[Fe_4S_4]^{2+/3+}$ redox couple of $[Fe_4S_4(SAd)_4]^{2-}$ in an aqueous PDACA solution was observed using a glassy carbon electrode, but the $[Fe_4S_4]^{+/2+}$ couple was obscured by the evolution of hydrogen.

new bands appeared at 440 and 290 nm upon electrochemical oxidation of $[Fe_4S_4(SAd)_4]^{2-}$ at +0.15 V *vs.* s.c.e. in the same solvent. In accordance with this, the absorption band of $HiPIP_{red}$ in the visible region shifts to longer wavelength upon oxidation of $HiPIP_{red}$ to $HiPIP_{ox}$.[8]

The electronic absorption spectrum of $[Fe_4S_4(SAd)_4]^{2-}$ in aqueous PDACA solution at pH 7.3 shows two bands at 440 and 290 nm (Figure 2b), similar to that in DMF. On the other hand, $[Fe_4S_4(SAd)_4]^{2-}$ in the same medium at pH 5.6 exhibits a weak band at 625 nm together with the LMCT bands at 420 and 290 nm (Figure 2c), and the spectral change between pH 7.3 and 5.6 occurred reversibly in the $[Fe_4S_4]^{2+}$ state. Furthermore, the electronic absorption spectrum of $[Fe_4S_4(SAd)_4]^-$ prepared by controlled-potential electrolysis of an aqueous PDACA solution of $[Fe_4S_4(SAd)_4]^{2-}$ at +0.15 V *vs.* s.c.e. also depended on the pH of the medium; three bands at $\lambda_{max.}$ 630, 420, and 280 nm were observed at pH 5.6, whereas these were shifted to $\lambda_{max.}$ 625(sh), 430, and 275 nm at pH 7.3. These observations suggest that protonation of $[Fe_4S_4]^{n+}$ (n = 2,3) takes place in aqueous PDACA solutions,[‖] since synthetic 4Fe–4S clusters undergo protonation reactions to exist as an equilibrium mixture between non-protonated and protonated clusters in an aqueous PDACA solution.[7]

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References

1 C. W. Carter, Jr., 'Iron-Sulfur Proteins,' vol. III, ed. W. Lovenberg, Academic Press, New York, 1977, p. 157—204.

2 C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1985, 323.

3 C. L. Hill, R. H. Holm, and L. E. Mortenson, *J. Am. Chem. Soc.*, 1977, **99**, 2549; R. E. Johnson, G. C. Papaefthymiou, R. E. Frankel, and R. H. Holm, *ibid.*, 1983, **105**, 7280; G. Christou, C. D. Garner, R. M. Miller, C. E. Johnson, and J. D. Rush, *J. Chem. Soc., Dalton Trans.*, 1983, 2363.

4 N. Ueyama, T. Terakawa, T. Sugawara, M. Fuji, and A. Nakamura, *Chem. Lett.*, 1984, 1287; T. O'Sallivan and M. M. Millar, *J. Am. Chem. Soc.*, 1985, **107**, 4097; V. Papaefthymiou, M. M. Millar, and E. Munck, *Inorg. Chem.*, 1986, **25**, 3010.

5 Y. Okuno, K. Uoto, O. Yonemitsu, and T. Tomohiro, *J. Chem. Soc., Chem. Commun.*, 1987, 1018.

6 B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 3523.

7 M. Masanaga, S. Kuwabata, K. Tanaka, and T. Tanaka, *Chem. Lett.*, 1986, 1531; M. Nakamoto, K. Tanaka, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, to be published.

8 K. Dus, H. De Klerk, K. Sletten, and R. G. Bartsch, *Biochim. Biophys. Acta*, 1967, **140**, 291.

[‖] In order to obtain information about the protonation of $[Fe_4S_4]^{3+}$, an e.s.r. measurement was carried out in DMF and in aqueous PDACA solutions at pH 7.3 and 5.6, respectively, containing $[Fe_4S_4(SAd)_4]^-$ at 77 K. However, no signal resulting from $[Fe_4S_4]^{3+}$ was observed at that temperature.

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