# PHOTOINDUCED ELECTRON TRANSFER WITH $[Fe_4S_4(SC_6F_5)_4]^{2-}$

## SUMIO NODA, SHIGETSOHI AONO and ICHIRO OKURA\*

Department of Bioengineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 (Japan)

(Received March 30, 1988; accepted April 15, 1988)

#### Summary

The  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  cluster with the electron-withdrawing terminal ligand, pentafluorobenzenethiolate, was synthesized and applied to the photoinduced electron transfer between  $Ru(bpy)_3^{2+}$  and  $[Fe_4S_4(SC_6F_5)_4]^{2-}$ . From the luminescence intensity of  $Ru(bpy)_3^{2+}$  in the presence of  $[Fe_4S_4(SC_6F_5)_4]^{2-}$ , static quenching was observed, and complex formation between  $Ru(bpy)_3^{2+}$  and  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  was proposed. The lifetime of  $Ru(bpy)_3^{2+}$  in the presence of  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  was measured by laser flash photolysis, and the quenching rate constant obtained was  $1.2 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ .

Fe<sub>4</sub>S<sub>4</sub> clusters have been widely found in a variety of functional proteins, including physiologically important electron carriers, ferredoxins and several enzymes. The redox property of the Fe<sub>4</sub>S<sub>4</sub> cluster plays a key role in the functions of these proteins. The synthetic clusters,  $[Fe_4S_4(SR)_4]^{2-}$ , have served as accurate models of these sites, and their physicochemical properties have been extensively characterized [1, 2]. The electron transfer reactions, however, have been seldom attempted thus far, except for the self-exchange reactions [3]. This is mainly because of the low reduction potentials of these synthetic clusters (<-1.0 V). In this letter we would like to describe the photo-induced electron transfer reaction using  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  with a relatively high reduction potential.

All procedures were performed under an argon atmosphere. The solvents were carefully purified before use by conventional methods.  $[Fe_4S_4-(SC_6F_5)_4]^{2-}$  was prepared by ligand substitution from  $[Et_4N]_2[Fe_4S_4(SBu^t)_4]$  and pentafluorobenzenethiol\*.  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  exhibited the characteristic weak shoulder bands at *ca*. 410 nm (ascribed to S—Fe charge transfer) and at *ca*. 340 nm.

<sup>\*</sup>Author to whom correspondence should be addressed.



Fig. 1. Relation between luminescence intensity vs.  $Fe_4S_4(SC_6F_5)_4^{2-}$  concentration;  $Ru(bpy)_3^{2+}: 5.90 \times 10^{-5} \text{ mol dm}^{-3}$ , solvent: DMF.

The cyclic voltammogram [4] of  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  (using tetraethylammonium perchlorate as supporting electrolyte, in acetonitrile) consisted of the reversible couple at  $E_{1/2}$ , -0.75 V vs. SCE which is ascribed to the 2- to 3- redox process. The reduction potential of  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  was thus considerably higher than the values of the conventionally known synthetic  $Fe_4S_4$  clusters.

In the luminescence measurements, the sample solution containing  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  and  $[\operatorname{Fe}_4\operatorname{S}_4(\operatorname{SC}_6\operatorname{F}_5)_4]^{2^-}$  (if included) was deaerated by repeated freeze-pump-thaw cycles. The luminescence intensity (an integration along the luminescence spectrum between 570 nm and 750 nm) was measured by a Hitachi-850 spectrometer. The excitation wavelength was 550 nm. The luminescence of  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  was quenched by  $[\operatorname{Fe}_4\operatorname{S}_4(\operatorname{SC}_6\operatorname{F}_5)_4]^{2^-}$ . The Stern-Volmer plot  $(I_0/I - 1 \operatorname{vs.} [\operatorname{Fe}_4\operatorname{S}_4(\operatorname{SC}_6\operatorname{F}_5)_4]^{2^-}$  concentration) is shown in Fig. 1. The luminescence intensity ratio strongly depended on  $[\operatorname{Fe}_4\operatorname{S}_4(\operatorname{SC}_6\operatorname{F}_5)_4]^{2^-}$  concentration and increased sharply with that concentration. No linear relation was obtained on the Stern-Volmer plot, showing that the luminescence was quenched statically. As  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  is positively charged, it may easily be complexed with negatively charged  $[\operatorname{Fe}_4\operatorname{S}_4(\operatorname{SC}_6\operatorname{F}_5)_4]^{2^-}$ . Since the photoexcited complex does not irradiate, static quenching may be observed.

The luminescence lifetime in the presence of  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  was also measured. The experimental procedure for the conventional laser flash photolysis is described elsewhere [5]. As the light source, a Nd-YAG laser (excitation wavelength 532 nm, pulse duration *ca.* 10 ns) was used, and the detection wavelength was 620 nm. Photoexcited  $Ru(bpy)_3^{2+}$  was quenched by  $[Fe_4S_4(SC_6F_5)_4]^{2-}$  (Fig. 2) and the Stern-Volmer plot of the lifetime is shown in Fig. 3. A good linear relation between the lifetime and  $[Fe_4S_4(SC_6F_5)_4]^{2-}$ 

<sup>\*</sup>Satisfactory elemental analysis was obtained; <sup>19</sup>F NMR ( $\delta$ , d<sub>6</sub>-MeCN, CF<sub>3</sub>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 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>), 340 nm (18000).



Fig. 2. Time dependence of luminescence intensity of  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  (5.90 × 10<sup>-5</sup> mol dm<sup>-3</sup>) in the absence (a) and presence (b) of Fe<sub>4</sub>S<sub>4</sub>(SC<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>2-</sup>.



Fig. 3. Stern-Volmer plot of quenching of  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  luminescence by  $\operatorname{Fe}_4S_4(\operatorname{SC}_6F_5)_4^{2^-}$ .

 $F_5_{4}$ <sup>2-</sup> concentration was observed, showing that the luminescence was quenched dynamically, as shown in the following reaction:

 $\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+,*}} + [\operatorname{Fe}_{4}\operatorname{S}_{4}(\operatorname{SC}_{6}\operatorname{F}_{5})_{4}]^{2^{-}} \longrightarrow \operatorname{Ru}(\operatorname{bpy})_{3}^{3^{+}} + [\operatorname{Fe}_{4}\operatorname{S}_{4}(\operatorname{SC}_{6}\operatorname{F}_{5})_{4}]^{3^{-}}$ 

From the Stern-Volmer plot, the quenching rate constant was obtained as  $1.2 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  which was close to that found in the diffusion-controlled process.

## Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 62612505 'Dynamic Interactions and Electronic Processes of Macromolecular Complexes' from the Ministry of Education, Science and Culture.

## References

- 1 R. H. Holm, Acc. Chem. Res., 10 (1977) 427.
- 2 J. M. Berg and R. H. Holm, in T. G. Spiro (ed.), Iron-Sulfur Proteins, Vol. 4, Wiley, New York, 1982, p. 3.

- 3 R. H. Holm, W. D. Phillips, B. A. Averill, J. Mayerle and T. Herskovitz, J. Am. Chem. Soc., 96 (1974) 2109; J. G. Reynolds, E. J. Laskowsky and R. H. Holm, *ibid.*, 100 (1978) 5315.
- 4 B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr. and R. H. Holm, J. Am. Chem. Soc., 96 (1974) 4159.
- 5 I. Okura, N. Kaji, S. Aono and T. Nishisaka, Bull. Chem. Soc. Jpn., 60 (1987) 1243.