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研究简报

高电势铁硫蛋白的模型化合物：2,4,6-三苯基苯硫酚的4Fe4S簇合物的合成与性质

孙为银*

（南京大学配位化学研究所，配位化学国家重点实验室，南京 210093）

上野隆史 上山宪一 中村 晃

（日本大阪大学理学部，丰中市 560，日本）

新型簇合物$(n\text{-}Bu_4N)_2[Fe_4S_4(tpbt)_4]$(tpbt=2,4,6-三苯基苯硫酚基)通过2,4,6-三苯基苯硫酚和$(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$在DMF(二甲基甲酰胺)中进行配体交换反应合成得到。该簇合物在CH_3CN溶液中的$[Fe_4S_4]^{3+/2+}$和$[Fe_4S_4]^{2+/1+}$的氧化还原电位分别为-0.14和-1.31 V vs SCE(甘汞电极)。这个结果显示具有庞大位阻的2,4,6-三苯基苯硫酚配体使得其4Fe4S簇合物的$[Fe_4S_4]^{3+}$态相对稳定。

关键词： 4Fe4S簇合物 铁硫蛋白 三苯基苯硫酚

A NOVEL 4Fe4S CLUSTER WITH A BULKY 2,4,6-TRIPHENYLBENZENETHIOLATE LIGAND AS A MODEL OF HIGH POTENTIAL IRON-SULFUR PROTEINS

Sun Weiyin

(*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing* 210093)

Ueno Takafumi Ueyama Norikazu Nakamura Akira

(*Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka* 560, *Japan*)

A novel cluster, $(n\text{-}Bu_4N)_2[Fe_4S_4(tpbt)_4]$(tpbt=2,4,6-triphenylbenzenethiolato), was synthesized by ligand-exchange reaction of $(n\text{-}Bu_4N)_2([Fe_4S_4(S\text{-}t\text{-}Bu)_4]$with 2,4-6-triphenylbenzenethiol in DMF. The cluster shows $[Fe_4S_4]^{3+/2+}$ and $[Fe_4S_4]^{2+/1+}$ redox potentials at -0.14 and -1.31 V vs. SCE, respectively in acetonitrile. The result suggests that the 3+ state of $[Fe_4S_4]$ core is stabilized relatively by the bulky tpbt ligand.

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* 通讯联系人。

第一作者：孙为银，男，33岁，教授；研究方向：金属酶和金属蛋白模型化合物的合成与性质研究。

Keywords: 4Fe4S cluster Iron-sulfur protein triphenylbenzenethiol

0 Introduction

The native iron-sulfur proteins with 4Fe4S clusters are believed to function as an electron transfer mediator in the biological system using $[Fe_4S_4]^{3+/2+}$ and $[Fe_4S_4]^{2+/1+}$ two redox couples. In order to understand the mechanism of electron transfer occurred in these native metalloproteins, many modelling compound studies have been carried out for each of $[Fe_4S_4]^{3+}$, $[Fe_4S_4]^{2+}$ or $[Fe_4S_4]^{1+}$ oxidation state[1~3]. Up to date, the synthesis of complexes with $[Fe_4S_4]^{2+}$ or $[Fe_4S_4]^{1+}$ core, such as $[Fe_4S_4(SPh)_4]^{2-}$, $[Fe_4S_4(SPh)_4]^{3-}$ *etc.*, has been succeeded[1,2], however, none of the one with $[Fe_4S_4]^{3+}$ core has been isolated yet, although the native high potential iron-sulfur proteins (HiPIP) with $[Fe_4S_4]^{3+}$ core are stable. Much attempt has been made to find a relatively stable model complex with $[Fe_4S_4]^{3+}$ core[3,4]. As results of these studies, the 4Fe4S clusters with a bulky ligand, for example, 2,4,6-trimethyl-benzenethiolate[4], 2,4,6-triisopropyl-benzenethiolate[4] and 1-adamantanethiolate[3], have been found to have a relatively stable $[Fe_4S_4]^{3+}$ core confirmed by electrochemical studies.

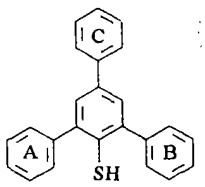

Fig. 1 Schemiatic drawing for the structure of 2, 4, 6- triphenylbenzenethiol (tpbt- H) ligand.

On the other hand, amino acid residues with aromatic ring as Tyr, Phe *etc.* have been found to be near the active site for native iron-sulfur proteins as HiPIP and rubredoxin from the X-ray analysis[5]. Such aromatic groups are suggested to play an important role in stabilizing the oxidized form of native metalloproteins[5] as well as rubredoxin model complexes[5]. In this paper, we report a novel 4Fe4S cluster with a bulky 2,4,6-triphenylbenzenethiolate ligand as shown in Fig. 1.

1 Experimental

1.1 Synthesis of $(n\text{-}Bu_4N)_2[Fe_4S_4(tpbt)_4]$

2,4,6-Triphenylbenzenethiol(tpbt-H) was synthesized from 2,4,6-triphenylaniline by modified procedures as reported in the literature[6a]. Analytical data of tpbt-H: Calcd for $C_{24}H_{18}S$: C, 85.17; H, 5.36; S, 9.47. Found: C, 85.92; H, 5.30; S, 9.22. m.p.: 144.0~144.5℃ (literature: 145.5~146.5℃[6]). Its 4Fe4S cluster, $(n\text{-}Bu_4N)_2[Fe_4S_4(tpbt)_4]$ was obtained by the ligand-exchange reaction between $(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$ (1.0 eq) and 2,4,6-triphenylbenzenethiol (tpbt-H) (4.2 eq) in *N*, *N'*-dimethylformamide (DMF) at room temperature. The cluster was purified by general procedures as reported for the cases of $[Fe_4S_4(2,4,6\text{-trimethylbenzenethiolate}_4]^{2-}$ and $[Fe_4S_4(2,4,6\text{-triisopropylbenzenethiolate})_4]^{2-}$[4]. Yield, ca 80%. The purity of the obtained cluster was checked by ^1H NMR spectroscopy. The integral ratio of the tpbt ligand protons vs the methyl protons of counter cation was 17 : 6 which is consistent with the composition of $(n\text{-}Bu_4N)_2[Fe_4S_4$

$(tpbt)_4]$, and no signal due to impurity was observed.

All operations including cluster synthesis and spectral measurements were carried out under argon atmosphere.

1.2 Physical measurements

Absorption spectra measurements were performed on a JASCO Ubest-30 spectrophotometer using a 1-mm quartz cell. The 400 MHz ^1H NMR spectra were measured on a JEOL GSX 400 NMR spectrometer. Cyclic voltammograms were recorded on a YANACO P-1100 instrument with a three-eletrode system: a glassy carbon working eletrode, a Pt-wire auxiliary eletrode and a saturated calomel eletrode (SCE). $[(n\text{-}Bu)_4N][ClO_4]$(100 mM) was used as a supporting eletrolyte. Potenticals were determined at room temperature vs a SCE as a reference.

2 Results and Discussion

The absorption spectrum of the synthesized cluster, $(n\text{-}Bu_4N)_2[Fe_4S_4(tpbt)_4]$, in DMF is shown in Fig. 2. An absorption maximum at 395 nm (ε: 37900) was observed. The reported 4Fe4S clusters with sterically hindered thiolate ligands exhibit absorptions at about 410 nm, *e. g.* $[Fe_4S_4$(2,4,6-trimethylbenzenethiolate)$_4]^{2-}$: 412 nm (ε: 22500), $[Fe_4S_4$(2, 4, 6-triisopropylbenzenethiolate)$_4]^{2-}$: 413 nm (ε: 26900)[4], while the parasubstituted thiophenolate cluster such as $[Fe_4S_4(S\text{-}C_6H_4\text{-}p\text{-}CH_3)_4]^{2-}$ shows an absorption maximum at 461 nm (ε: 18600) in DMF[7]. Thus the $[Fe_4S_4(tpbt)_4]^{2-}$ shows a quite blue-shifted absorption maximum. This is considered to be caused by the bulkiness of two phenyl groups A and B (see Fig. 1) at the ortho and ortho′-positions of the central phenyl group, and by the electron-withdrawing phenyl group C (see Fig. 1) at the paraposition.

The existence of 4Fe4S core in the cluster was confirmed by core extrusion method as shown in Fig. 2 (the dashed line)[8]. The formation of 4Fe4S/tpbt cluster is also supported by ^1H NMR spectral measurements. No signal at about 2. 6 ppm was observed in the ^1H NMR spectrum of the synthesized 4Fe4S/tpbt cluster in acetonitrile-d_3 at 30℃ which is due to the *t*-Bu protons of $(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$[9]. The result indicates the completed ligand-exchange reaction between S-*t*-Bu and tpbt.

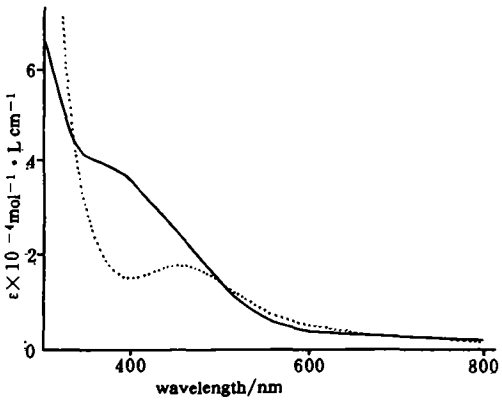

Fig. 2　Absorption spectra of $[Fe_4S_4(tpbt)_4]^{2-}$ in DMF (solid line) and after additon of excess thiophenol (dashed line).

The redox potential of the cluster was investigated by measurement of the cyclic voltammogram in acetonitrile. As shown in Fig. 3, the synthesized cluster gives a quasi-reversible redox couple of $[Fe_4S_4(tpbt)_4]^{2-/1-}$ at -0. 14 V vs. SCE ($E_{p,a}$=-0. 10 V, $E_{p,c}$=-0. 18 V, $\frac{i_{p,c}}{i_{p,a}}$=1. 07), while the redox potential of $[Fe_4S_4(tpbt)_4]^{3-/2-}$ is observed at

-1.31 V vs. SCE ($E_{p,a}$=-1.24 V, $E_{p,c}$=-1.38 V) with poor reversibility, $[Fe_4S_4$(2, 4, 6-trimethylbenzenethiolate)$_4]^{2-}$ has been reported to show 2-/1- and 3-/2- redox potentials at 0.00 V and -1.20 V vs. SCE in acetonitrile, respectively[10]. In this case, both the 2-/1- and 3-/2- redox couplex are quasi-reversible, but the reversibility of 2-/1- redox couple is poorer than that of the 3-/2- one. Thus, the result of $[Fe_4S_4(tpbt)_4]^{2-}$ indicates that, when the substituents at 2,4,6-positions become larger (phenyl groups instead of methyl groups), the reversibility of the 2-/1- redox couple is increased while that of the 3-/2- one is decreased. This trend has also been observed for the case of $[Fe_4S_4$(2,4,6-triisopropylbenzenethiolate)$_4]^{2-}$[4]. In conclusion, our results also support that the bulkiness of the ligands is needed for the stabilization of the oxidation state of 4Fe4S cluster.

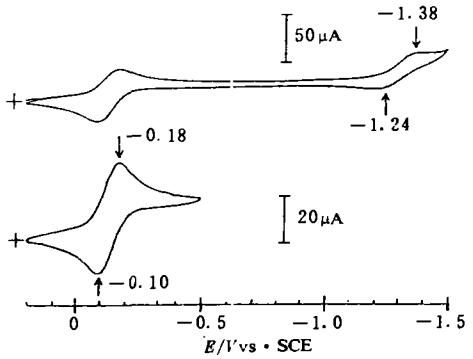

Fig. 3 Cyclic voltammograms of $[Fe_4S_4(tpbt)_4]^{2-}$ in acetonitrile at glassy carbon electrode, supporting electrolyte N(*n*-Bu)$_4ClO_4$: 100 mmol · L^{-1} and scan rate: 100 mVs^{-1}.

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