

纳米银对表面吸附镝配合物的荧光增强效应研究

王悦辉¹ 周 济^{*2} 王 婷²

(¹ 电子科技大学中山学院化学与生物系, 中山 528402)

(² 清华大学材料科学与工程系, 新型陶瓷与精细工艺国家重点实验室, 北京 100084)

摘要: 研究了不同粒径的纳米银对镝配合物(乙二胺四乙酸配合物)的光谱学性质影响。当配合物溶液的 pH 值范围为 4.0~6.0 时, 加入纳米银, 可观察到大量的纳米银聚集体形成, 而在吸收光谱的长波处出现一个新的吸收峰, 随着纳米银浓度的增加, 该吸收峰逐渐红移, 同时, 镝配合物的荧光强度增强。实验结果表明, 纳米银粒子对镝配合物的荧光增强效应及荧光增强因子与纳米银粒子的浓度和粒径密切相关。随着纳米银浓度的增加, 配合物的荧光强度先增强而后又逐渐降低。小粒径的纳米银对镝配合物的荧光增强因子较小。本文从纳米银粒子的聚集效应、局部电磁场增强效应及光吸收效应等方面探讨了纳米银对表面吸附镝配合物的荧光增强效应机理。

关键词: 纳米银; 镝配合物; 荧光增强效应; 局部表面等离子体共振

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Fluorescence Enhancement of Dysprosium Complex by Binding to Silver Nanoparticles

WANG Yue-Hui¹ ZHOU Ji^{*2} WANG Ting²

(¹Department of Chemistry and Biology, Zhongshan Institute, University of Electronic Science and Technology of China, Zhongshan, Guangdong 528402)

(²State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084)

Abstract: The photoluminescent properties of dysprosium complex (ethylenediamine tetra acetate) were investigated in the presence of different sized Ag nanoparticles. The formation of nanoparticles aggregates and a new absorption band at longer wavelength region were observed upon the addition of Ag nanoparticles when the pH value of the complex solution was 4.0~6.0. With the increase of the concentration of Ag nanoparticles, the peak at long wavelength was red-shifted, at the same time, enhancement of the emission intensity for the complex solution containing Ag nanoparticles was observed. The enhanced fluorescence of the complex and the enhancement factors were dependent on the concentration and size of Ag nanoparticles. With increasing Ag nanoparticles concentration enhancement factor first increases and then decreases. The enhancement factor of small Ag nanoparticles is lower than that of large Ag nanoparticles, meanwhile, the enhancement factor of small Ag nanoparticles can reach the maximum in lower Ag amount condition. The enhancement effect was discussed in terms of the effects of nanoparticle aggregates, the local electromagnetic field enhancement effect and optical absorption due to surface plasmon resonance.

Key words: Ag nanoparticles; dysprosium complex; luminescence effect; localized surface plasmons resonance

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* 通讯联系人。E-mail: zhouji@mail.singhua.edu.cn

第一作者: 王悦辉, 女, 33 岁, 博士; 研究方向: 信息功能材料及光电材料。

The lanthanide complexes are of both fundamental and technological interest because of their large Stokes shifts, narrow emission bandwidths, and long emission lifetimes. Due to these characteristics, they are widely used in high-sensitivity immunoassays and in DNA hybridization assay^[1-3]. Recently, growing attention has been paid to the fluorescence enhancement of fluorophores, based on the metal-enhanced fluorescence (MEF)^[4-9]. It is widely accepted that for optical processes the primary role of metallic nanostructures and rough metallic surface is to enhance the local electromagnetic field via the localized plasmon resonance, and thus increase the excitation and emission of light^[4,5].

Recent reports have shown enhanced/quenched fluorescence of lanthanide complexes when they close to the chemically deposited Ag islands film^[6,7]. Wu et al.^[8] studied the fluorescent properties of Eu^{3+} ions by depositing europium tetracycline onto thin polyvinyl alcohol films coated with Ag nanoparticles and observed a 16-fold enhancement in lanthanide complex fluorescence. Selvan et al.^[9] reported the fluorescence enhancement from Eu^{3+} ions doped silica gels containing adsorbed Ag islands and proposed that the most possible mechanism for the fluorescence enhancement was the local field enhancement around Eu^{3+} ions, due to the electronic plasmon resonance of Ag islands. Nabika et al.^[10] reported enhancing and quenching functions of silver nanoparticles on the luminescent properties of europium complex in N,N -dimethylformamide. They noticed that the nanoparticles concentration dependence of the luminescent intensity was the result of a delicate balance between an enhancing and a quenching effect of the silver nanoparticles.

In this work, an effect of Ag nanoparticles on the fluorescent properties of dysprosium (Dy^{3+}) complex in the solution system was observed, the dependence of the enhancement on Ag concentration and size was studied.

1 Experimental

1.1 General procedure

AgNO_3 (99.8%), NaBH_4 (98.0%), sodium citrate dihydrate (99.0%) and HNO_3 (69.0%) are analytical

grade, from Beijing Chemical Reagent Industries. Dy_2O_3 (99.95%) was purchased from Alfa Aesar. All chemicals were used as received. Throughout the experiment deionized water was used.

The Electron micrographs were obtained with a JEM-200CX transmission electron microscopy (TEM) with acceleration voltage of 200 kV. The specimens were prepared by dropping the mixture solution of dysprosium complex and silver colloid on the carbon-coated grids, and dried. Electrokinetic measurement of Ag nanoparticles was evaluated with a P/ACE MDQ electrophoresis analyzer. Ag nanoparticles were negatively charged. UV-Vis absorption spectra were recorded at room temperature on a ThermoSpectronic UNICAM UV-500 PC spectrophotometer using a quartz cuvette with a 1 cm optical path at room temperature. Luminescence measurements were recorded at room temperature using a Cary Eclipse spectrofluorometer with a 90° configuration. The concentration of Ag colloidal solution (the number of Ag nanoparticles in unit volume (n , particles $\cdot \text{L}^{-1}$)) was measured by Inductively Coupled Plasma Emission Spectrometry (ICP, Profile, Leeman, USA).

1.2 Preparation

The dysprosium complex was synthesized by dissolving EDTA into $\text{Dy}(\text{OH})_3$ with a molar ratio of EDTA/ $\text{Dy}^{3+}=1/2$. $\text{Dy}(\text{OH})_3$ was prepared through the following processes. Firstly, dysprosium oxide (Dy_2O_3) was dissolved by HNO_3 ($10 \text{ mol} \cdot \text{L}^{-1}$) to obtain $\text{Dy}(\text{NO}_3)_3$ solution, and then a certain amount of ammonia (molar ratio of the $\text{NH}_3 \cdot \text{H}_2\text{O}$ to Dy^{3+} at 1/1) was dropped into the solution. Finally, $\text{Dy}(\text{OH})_3$ precipitates were obtained by centrifugation to remove the free ions (NO_3^- , NH_4^+). Two sets of Ag nanoparticles with mean diameters of 6.8 and 41.6 nm were synthesized by a modified Murray's and Meisel's methods, respectively^[11,12], and strong absorption peaks were noted at around 397 nm and 420 nm, respectively. The samples for the optical measurements were prepared by mixing the Dy^{3+} complex solution and the Ag colloid (Dy^{3+} -Ag) while keeping the final concentration of Dy^{3+} ion at $6.40 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$.

2 Results and discussion

The UV-Vis absorption spectra of Dy^{3+} complex solution, Ag colloid ($d=6.8$ nm) and the mixture solution of Dy^{3+} -Ag with different amounts of Ag colloid are shown in Fig.1A. Upon addition of Ag nanoparticles into Dy^{3+} complex solution, the color of the solution immediately changed to pinkish red, accompanying the increase of absorption peaks at 320~410 nm and the appearance of a new absorption band around 410~800 nm (curve c~g in Fig.1A). The appearance of the new band at longer wavelength region reveals the formation of nanoparticles aggregates in the solution, indicating the function of the dysprosium complexes as linker molecules, and the complexes are expected to be incorporated in the particle aggregates^[13]. The increase of absorbance becomes more obvious with the increase of the concentration of Ag colloid. Meanwhile, for the Ag colloid the peak at long wavelength is red-shifted from 535 to 561 nm with the increase of the concentration of the Ag nanoparticles, which may

indicate that the peaks at 320~410 nm are fixed no matter how particle size is increased.

It is important to note that only when the pH value of the solution is 4.0~6.0, can color and spectral change be observed. When the pH value is less 4.0, the color of the solution changes to pinkish red, accompanied by precipitation. When the pH value is more than 6.0, no color and spectrum changes are observed. The effect of the ambient pH value of Dy^{3+} complex solution on Ag nanoparticles is attributed to the results of the intermolecular hydrogen bonding ability of carboxylic acid, namely, EDTA. When the ambient pH value of Dy^{3+} complex solution is 4.0~6.0, Dy^{3+} complexes are partially ionized, and carboxylic acid groups not only bind to the surface of Ag nanoparticles but also further interact between Dy^{3+} complexes through intermolecular hydrogen bonding to yield nanoparticles assemblies. The representative TEM micrographs of Ag nanoparticles and Ag nanoparticles added into Dy^{3+} complex solution is shown in Fig.1B and 1C, image inserted in B is the XRD pattern of Ag nanoparticles.

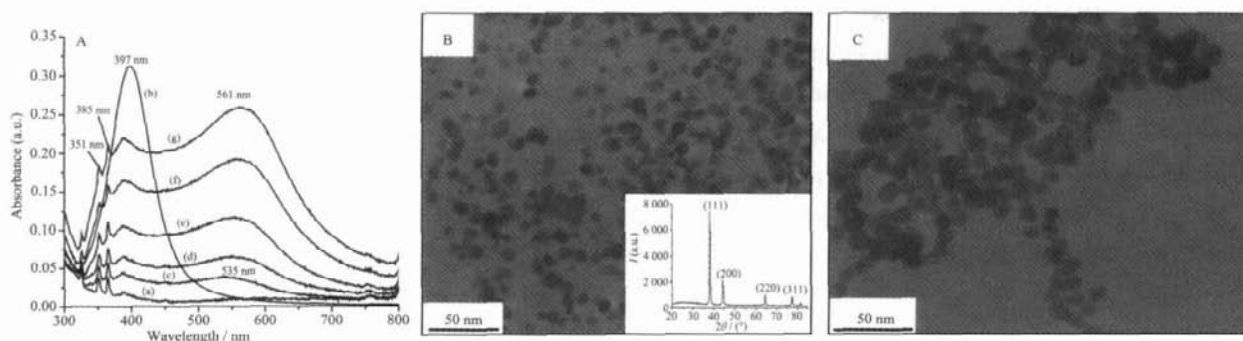


Fig.1 (A) Absorption spectra of Dy^{3+} complex solution (a), Ag colloid (b), and the mixture solution of Dy^{3+} -Ag solution, and (c)~(g) the mixture solution containing the different contents of Ag 1.04, 4.16, 8.32, 15.60 and 26.00 ($\times 10^{15}$ particle $\cdot \text{L}^{-1}$); (B) TEM images of Ag nanoparticles and (C) Ag nanoparticles add into Dy^{3+} complex solution when the pH value of the solution is 5.4

The excitation spectra of Dy^{3+} complex solution and the mixture solution of Dy^{3+} -Ag are shown in Fig.2. It is known that the solution containing Dy^{3+} ion has two fluorescence emission peaks at 485 and 576 nm corresponding to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions of Dy^{3+} ion, respectively. It is interesting to note that the corresponding excitation peak at 351 nm is enhanced when the detection wavelength is at 485 nm. However, only little change of the excitation peak at

351 nm is observed when the detection wavelength is at 576 nm, as shown in Fig.2.

The influence of the existence of Ag nanoparticles on the emission from Dy^{3+} complex solution was investigated. The emission spectra of Dy^{3+} complex solution and the mixture solution of Dy^{3+} -Ag containing 8.32×10^{15} particle $\cdot \text{L}^{-1}$ Ag nanoparticles with mean diameter of 6.8 nm excited at 351 nm are shown in Fig.3. Two emission peaks centered at 485 nm and 576 nm,

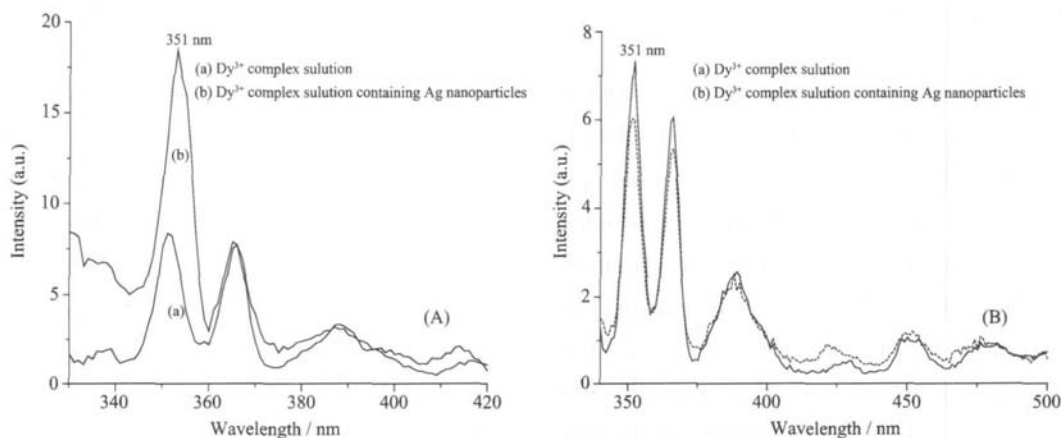


Fig.2 Excitation spectra of Dy^{3+} complex solution and the mixture solution of Dy^{3+} -Ag containing $8.32 \times 10^{15} \text{ particle} \cdot \text{L}^{-1}$ Ag nanoparticles with mean diameter of 6.8 nm at detection wavelength of 485 nm (A) and 576 nm (B)

assigned to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transitions, are observed. For the mixture solution of Dy^{3+} -Ag, the emission intensity at 485 nm is enhanced under the excitation at 351 nm (Fig.3). However, the emission intensity at 576 nm almost has no change. It is consistent with the changes of excitation spectrum. The enhanced fluorescence should derive from the local electromagnetic field enhancement around Dy^{3+} ions owing to the induced surface plasmon resonance of Ag nanoparticles, which has been observed in other systems^[14–23]. As the excitation wavelength (at around 351 nm) is close to the resonance mode of the surface plasmon in silver nanoparticle, we propose that it is possible for the luminescent centers of Dy^{3+} ions to be strongly excited through the induced electromagnetic field. Similarly,

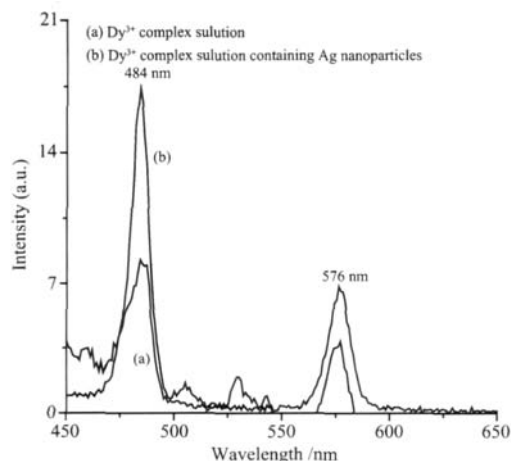


Fig.3 Emission spectra of Dy^{3+} complex solution and the mixture solution of Dy^{3+} -Ag containing $8.32 \times 10^{15} \text{ particle} \cdot \text{L}^{-1}$ Ag nanoparticles with mean diameter of 6.8 nm (excitation=351 nm)

the energy corresponding to transition between ${}^4\text{F}_{9/2}$ to ${}^6\text{H}_{15/2}$ is closer to the surface plasmon resonance frequency than that of ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$, so the former obtains a stronger enhancement.

It is noteworthy that the luminescence enhancement by metallic nanoparticles is strongly dependent on the distance from the fluorophore to the metallic surface, the nanoparticle size and shape and concentration and surface, environmental parameters, and binding-state between the fluorophore and metallic surface, and so on^[15–21]. In our study, the luminescence enhancement is observed only when the pH value of the solution is 4.0 ~6.0. We believe that luminescence enhancement is relative to the aggregates formation. When several particles approach closely, the electromagnetic fields from them are expected to be overlapped to result in a stronger field, leading to a stronger surface enhanced fluorescence^[23]. Furthermore, we observed a new absorbance band in the absorption spectrum in the present system. Such an absorbance could overcome a competitive quenching to induce a luminescence enhancement. As mentioned above, Dy^{3+} complexes are expected to be incorporated into nanoparticle aggregates, and thus the luminescence is effectively enhanced in the present system. The aggregation of particles brings about a luminescence enhancement to some extent, indicating that the enhancement on the aggregated particle could not be explained by an ordinary competitive mechanism of quenching and enhancement.

The enhancement factor, defined as the integrated emission intensity (the background is eliminated) ratio of the mixture solution of Dy^{3+} -Ag to Dy^{3+} complex solution at 485 nm emission wavelength, is illustrated against the concentration of Ag nanoparticles in Fig.4. We can see that the enhancement factor increases at a certain Ag concentration and then decreases with the increasing of Ag nanoparticles concentration, and two samples show different maxima enhancement factors and different Ag nanoparticles concentrations at which the intensity reaches the maximum. For the mixture solution of Dy^{3+} -Ag with mean diameter of 6.8 nm, the maximum enhancement factor reaches to 2.42 at Ag nanoparticles concentration up to $9.36 \times 10^{15} \text{ particle} \cdot \text{L}^{-1}$, while for the mixture solution of Dy^{3+} -Ag with mean diameter of 41.6 nm, the maximum enhancement factor reaches to 2.74 at Ag nanoparticles concentration up to $2.15 \times 10^{14} \text{ particle} \cdot \text{L}^{-1}$. When Ag nanoparticles are added into Dy^{3+} complex solution, some Dy^{3+} complexes are localized or closed to the surface of Ag nanoparticles, so Dy^{3+} complex solution fluorescence intensity is enhanced through the local electromagnetic field enhancement around Dy^{3+} ions owing to the induced surface plasmon resonance of Ag nanoparticles. With increasing of Ag nanoparticles, more and more Dy^{3+} complexes are localized or closed to Ag nanoparticles until saturated. Further increasing of Ag nanoparticles, re-absorption of surface plasmon resonance of Ag nano-

particles is dominant, so intensity gradually decreases. Therefore, it is deduced from concentration dependence that the observed enhancement factor is the result from delicate balance of the local electromagnetic field enhancement and re-absorption of surface plasmon resonance. In addition, surface area of small Ag nanoparticles is higher than that of large Ag nanoparticles, so the enhancement factor of small Ag nanoparticles can reach the maximum in lower Ag amount conditions when Dy^{3+} complexes amount is constant. The effectiveness of metallic nanoparticles for enhancement phenomenon is widely known and explained about mechanism^[5,8,17-23]. However, it is very difficult to predict the effectiveness in different systems. Only in specifically experimental conditions the effectiveness of metallic nanoparticles for enhancement phenomenon is observed. Since the enhancement effect strongly depends on different experimental conditions systematic studies are required to elaborate the relation between the local electromagnetic field enhancement and surface plasmon resonance with respect to the condition of Ag nanoparticles for further improvement of overall enhancement effect and is currently under investigation in our group.

3 Conclusions

In conclusion, the effects of Ag nanoparticles on the fluorescent properties of the Dy^{3+} complex (ethylenediamine tetraacetate) in the solution system have been studied. When the pH value of the complex solution is 4.0 ~6.0, the formation of nanoparticles aggregates and the appearance of a new absorption band at longer wavelength region are observed, and with the increase of the concentration of the Ag nanoparticles, the peak at long wavelength is red-shifted, at the same time, enhancement of the emission intensity for the complex solution containing Ag nanoparticles is observed. The enhanced fluorescence of the complex and the enhancement factors are dependent on the concentration and size of Ag nanoparticles. With increasing Ag nanoparticles concentration enhancement factor first increases and then decreases. The enhancement factor of small Ag

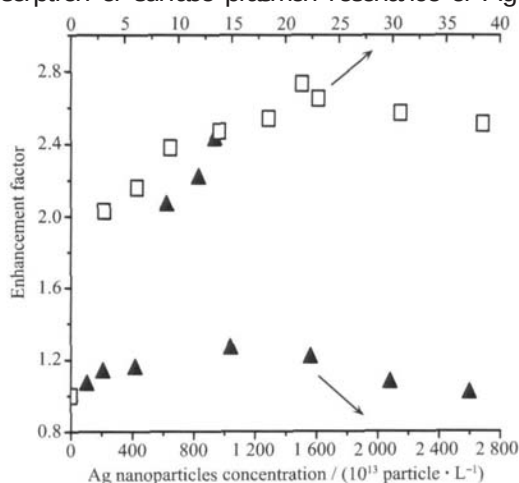


Fig.4 Enhancement factors of Dy^{3+} complex solutions containing different diameters Ag nanoparticles ($d=6.8 \text{ nm}$ (▲) and 41.6 nm (□)) at different silver nanoparticles concentrations

nanoparticles is lower than that of large Ag nanoparticles, meanwhile, the enhancement factor of small Ag nanoparticles can reach the maximum in lower Ag amount conditions. The enhancement effect is discussed in terms of the effects of nanoparticle aggregates, the local electromagnetic field enhancement effect and optical absorption due to surface plasmon resonance.

References:

- [1] Lamture J B, Wensel T G. *Bioconjugate Chem.*, 1995,6:88~92
- [2] Lakowicz J R, Maliwal B P, Malicka J, et al. *J. Fluorescence*, 2002,12:431~437
- [3] Horrocks W, Dew J, Collier W E. *J. Am. Chem. Soc.*, 1981, 103:2856~2862
- [4] Petit L, Griffin J, Carlie N, et al. *Materials Lett.*, 2007,61: 2879~2882
- [5] Zhang J, Lakowicz J R. *J. Phys. Chem. B*, 2005,109:8701~8706
- [6] Chowdhury M H, Lakowicz J R, Geddes C D, et al. *Appl. Phys. Lett.*, 2006,88:173104-1~173104-3
- [7] Lakowicz J R. *Anal. Biochem.*, 2005,337:171~194
- [8] Wu M, Lakowicz J R, Geddes C D. *J. Fluorescence*, 2005,15: 53~59
- [9] Selvan S T, Hayakawa T, Nogami M. *J. Phys. Chem. B*, 1999, 103:7064~7067
- [10] Nabika H, Deki S. *J. Phys. Chem. B*, 2003,107:9161~9164
- [11] Templeton A C, Cliffl D E, Murray R W. *J. Am. Chem. Soc.*, 1999,121:7081~7089
- [12] Lee P C, Meisel D. *J. Phys. Chem.*, 1982,86:3391~3395
- [13] Zhang P X, Fang Y, Wang W N. *J. Raman Spectrosc.*, 1990, 21:127~131
- [14] Chowdhury M H, Malyn S N, Aslan K, et al. *J. Phys. Chem. B*, 2006,110:22644~22651
- [15] Marco M, Nelsi Z, Luca P, et al. *J. Am. Chem. Soc.*, 2007, 129:2418~2419
- [16] Gryczynski Z, Borejdo J, Calander N. *Anal. Biochem.*, 2006, 356:125~131
- [17] Haes A J, Chang L, Kleing W L, et al. *J. Am. Chem. Soc.*, 2005,127:2264~2271
- [18] Ipe B I, Yoosaf K, Thomas K G. *J. Am. Chem. Soc.*, 2006,128: 1907~1913
- [19] WANG Yue-Hui (王悦辉), ZHOU Ji (周 济), SHI Shi-Kao (石士考). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, 2006,22(9):1578~1584
- [20] Aslan K, Holley P, Geddes C D. *J. Immunological Methods*, 2006,312:137~147
- [21] Borejdo J, Gryczynski Z, Calander N, et al. *Biophys.*, 2006, 91:2626~2635
- [22] Hayakawa T, Selvan S T, Nogami M. *Appl. Phys. Lett.*, 1999, 74:1513~1515
- [23] Hayakawa T, Furuhashi K, Nogami M. *J. Phys. Chem. B*, 2004,108:11301~11307