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DISPERSED THIN FILMS OF MIXED-VALENCE ONE-DIMENSIONAL TETRANUCLEAR PLATINUM COMPLEX AND THEIR OPTICAL PROPERTIES

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Abstract Transparent films of one-dimensional tetranuclear platinum complex, which has some mixed-valence states, was successfully prepared. Alumina gel and poly vinyl alcohol (PVA) were tested their suitabilities for a matrix. In the alumina matrix, their absorption spectra show that the Pt complex exists as the mixture with various valence states. On the contrast, in the PVA matrix, the absorption spectrum of the complex is unchanged from its solute sample state. THG properties were also investigated for their thin films.

INTRODUCTION

Many one-dimensional polynuclear complexes are subjects of considerable interest, because they have more or less electrical interactions between metals. We have already reported formations of linear metal chains in the thin film of metal complexes and their considerably large optical nonlinearities.[1] They originate from delocalized electrons in linear chain metals. Among such polynuclear complexes, especially, the complex having mixed valence metals have the intervalence transition. Thus, it is expected they have some optical functions. So-called "Platinum blue" complex is a class of mixed valence complexes having Pt(II) and Pt(III) in a one-dimensional tetranuclear chain structure. It can be easy for these to be controlled the valence states of Pt metals by the chemical technique.[2] They are particularly interesting, when the relationship between the electrical states in the one-dimensional metals and their optical properties is studied.

One of methods for applying such materials as the optical devise is to disperse them in the matrix. Generally, in the case of the metal complex / polymer system, it is known that some aggregation of complexes occurs in the matrix because such a solvent as well-dissolved both complexes and polymer matrixes is limited. However, the Pt complex soluble in both H_2O and some organic solvents was used in this study. And it was attempted to prepare the Pt complex-dispersed transparent film by the use

of organic or inorganic polymer as the matrix, and consider about their suitabilities for a matrix. Furthermore, for the preliminary study, third harmonic generation measurement was performed to estimate third-order nonlinear optical property of them.

EXPERIMENTAL

One-dimensional tetranuclear platinum complex used in this study is called pivalamide blue. The chemical structure is shown in Figure 1. This has four platinum metals, three Pt(II) and one Pt(III), connected linearly by four amidate bridgings and one Pt-Pt bond. The synthetic procedure and crystallographic data of it will be reported elsewhere.[3]

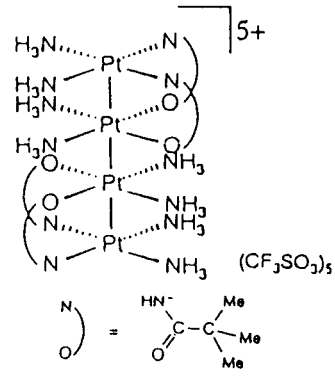

FIGURE 1 Chemical structure of pivalamide blue.

Alumina gel and poly vinyl alcohol (PVA) were used as the matrix. All chemicals to prepare films for dispersing of the complex were commercial grade and used without further purification. Alumina gel films were prepared by the use of the sol-gel method,[4] except of the use of nitric acid for the peptization process.[5] This method enables to produce metal oxide glasses without the high temperature treatment. The concentration of Al^{3+} ion in the sol was 0.84M. The molar concentration of aqueous solution of Pt complex used for the preparation of films was 4.87×10^{-3}M. The solution of Pt complex and alumina sol were mixed in the various contents and casted on quartz plates at atmosphere. For preparing pivalamide blue / PVA thin films, both dimethyl formamide (DMF) solutions of the Pt complex (9.8 g/l) and PVA (18.4 g/l) was mixed, and then the (1:1) mixture was casted on quartz plate at atmosphere.

The optical absorption spectra of samples were taken by Shimadzu UV-3100 spectrophotometer. Their measured wavelength ranges 200 nm-2400 nm. The film thickness were determined on a Tencor Alpha-step 300 surface profilometer.

RESULTS AND DISCUSSIONS

Pivalamide blue / Alumina

On dissolving pivalamide blue in water, the color of solution showed green. A day after, it turned yellow. If it is much more dilute, turned yellow at once. It has been reported the complex occurs both the reduction and oxidation reactions in the solution

easily dependent on its pH and coexisting species.[2] These phenomena can be investigated by absorption spectroscopic analysis, because this complex contains mixed-valence Pt metals and shows strong bands due to their intervalence transition. Figure 2 shows optical absorption spectra of both green and yellow solutions. A strong band at 680 nm was observed in the spectrum of the green solution. About the yellow solution, 680 nm band disappeared and weak band appeared at 240 nm complex. According to the former work,[2,6] 680 nm band was ascribed to $[Pt(II)_3Pt(III)]^{9+}$ ion, and 240 nm band is ascribed to $[Pt(II)_2]^{4+}$ ion. Thus obtained spectral change shows the reaction(1) have occurred.

$$[Pt(II)_3Pt(III)]^{9+} \xrightarrow{\text{water}} [Pt(II)_2]^{4+} \qquad (1)$$

On adding green aqueous solution of $[Pt(II)_3Pt(III)]^{9+}$ to alumina sol, first it turned reddish violet and then yellow. If adding yellow aqueous solution of $[Pt(II)_2]^{4+}$, drastic color change could not be observed. Figure 3 show optical absorption spectrum of Pt complexes dispersed in the alumina sol (yellow). Absorption bands at 300 nm and 375 nm were seen. When it took the color of reddish violet, another weak band at 495 nm was also seen. It was known that 300 nm band and 375 nm band were ascribed to $[Pt(III)_2]^{6+}$ ion and 495 nm was ascribed to $[Pt(II)_2Pt(III)_2]^{10+}$ ion.[2] In this case, for the original alumina sol had acidity (pH=4.89), they were oxidized by oxygen in the air and at last $[Pt(III)_2]^{6+}$ complex was formed(2).[2]

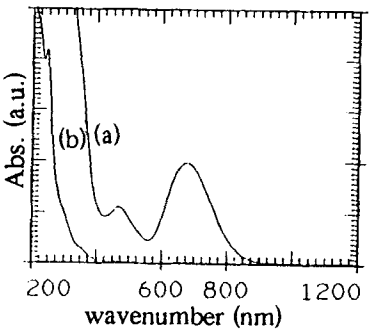

FIGURE 2 The absorption spectra of aqueous pivalamide blue. (a) green, (b) yellow.

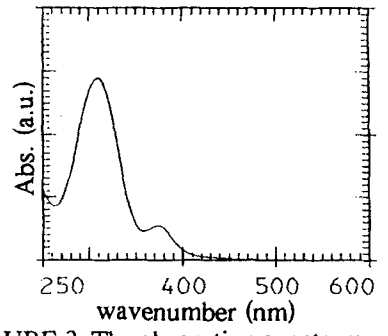

FIGURE 3 The absorption spectrum of pivalamide blue / alumina sol (yellow).

$$\begin{array}{ccc} & \xrightarrow{O_2} & \\ [Pt(II)_2]^{4+} & & [Pt(III)_2]^{6+} \\ \downarrow O_2 & O_2 \quad \uparrow O_2 & \\ [Pt(II)_3Pt(III)]^{9+} & \longrightarrow & [Pt(II)_2Pt(III)_2]^{10+} \end{array} \qquad (2)$$

The yellow $[Pt(III)_2]^{6+}$ complex alumina was casted on a quarts plate at atmosphere. The thin film with high transparency and homogeneity could be obtained. However, their colors were not yellow but variable against the ratio of the complex and alumina. While high contents of the complex gave a blue film, low contents gave a reddish violet film as shown in Table I. Figure 4 shows optical absorption spectra of Pt complex / alumina thin films with the reddish violet (a) and blue (b) colors. Two bands at 520 nm and 736 nm were observed in the spectrum of (a). These bands seem to indicated the existence of $[Pt(II)_2Pt(III)_2]^{10+}$ and $[Pt(II)_3Pt(III)]^{9+}$, respectively. Large red shifts of both wavelengths from those in aqueous solutions may be due to the local environmental effect of the alumina networks. On the other hand, the strong and broad bands at 800-1,100 nm appeared in the blue film. It was apparent to be different from the original pivalamide blue from the comparison to their spectra shown in Figure 2. It might be formed other complex having the longer Pt metal chain.[7] In conclusion, although some transition on its valent states occurred during the preparation process, highly transparent film with well dispersed metal complexes could be obtained. The dispersed complexes are composed of the mixture with various valence states. Thus some electrochemical treatments may be required in order to obtain the film of the complex with a single valence state.

TABLE I The difference of colors against the ratio of Pt complex / alumina.

Run No.	complex/alumina g/g	color
1	$9.37X10^{-2}$	reddish violet
2	$1.56X10^{-1}$	reddish violet
3	$4.67X10^{-1}$	violet
4	$9.37X10^{-1}$	blue

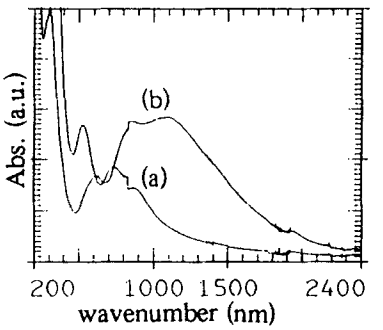

FIGURE 4 The absorption spectra of Pt complex / alumina thin films. (a) reddish violet, (b) blue.

Pivalamide blue / PVA

Next, we attempted to make the thin film of Pt complex by using the poly vinyl alcohol

(PVA) as an organic matrix. The mixed DMF solution of the complex and PVA was casted on the quartz plate at atmosphere. The thin film with high transparency and homogeneity could be obtained. The concentration of Pt complex in this film was 34.8% w/w.

Figure 5 shows the optical absorption spectrum of Pt complex / PVA thin film. A strong absorption band appeared at 680 nm. This spectrum is similar to that of green aqueous solution of pivalamide blue showed in Figure 2. This indicated that the complex in PVA film kept its valence state and dispersed in the polymer network. Thus it was found that this system was useful for making the mixed-valence tetranuclear Pt complex-dispersed polymer thin film.

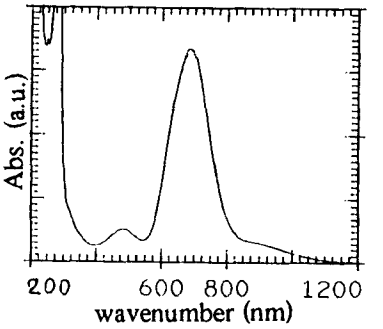

FIGURE 5 The absorption spectrum of pivalamide blue / PVA thin film.

For the preliminary study to estimate the third-order nonlinear optical susceptibility $\chi^{(3)}$ of pivalamide blue, THG Maker fringe measurements of pivalamide blue / PVA film obtained were performed. THG measurements were carried out 1.5-1.8 μm of fundamental wavelength.[1] The $\chi^{(3)}$ values of Pt complex / PVA film at various third harmonic wavelengths are showed in Table II. It was found that third harmonic generations around the absorption band at 680 nm were more intense. It indicated a large resonance effect was obtained near the 680 nm band.

About the estimation of $\chi^{(3)}$ of pivalamide blue itself, it is in progress of the preparation of Pt complex / PVA films with various contents and their THG measurements for the extrapolation of $\chi^{(3)}$ value to [Pt complex / PVA] ~ ∞.

CONCLUSION

It has been demonstrated that the transparent thin film of pivalamide blue could be obtained by using polymer matrixes. Because the complex was well soluble to both water and organic solvents, it could disperse homogeneously. However, in water system, both reduction and oxidation reactions occur easily depend on its pH or coexisting species. These resulted in the formation of the complex with various valence states in the alumina glass. In the organic polymer, it is noticeable to be able to disperse

the complex without using water. As the result, the thin film of the complex with highly transparent enough to study their optical properties could be successfully prepared without changing their mixed-valence states.

TABLE 2 The absorption coefficients α and the third-order nonlinear susceptibilities $\chi^{(3)}$ of pivalamide blue / PVA film. The thickness of this film is 5.68 μm.

wavelength / nm	α /cm^{-1}	$\chi^{(3)}$ x10^{13} / esu
600	2238	2.049
580	1241	2.066
540	611	2.058
500	887	0.995

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