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Takehito Kodzasa [a], Toshihide Kamata [a], Hirobumi Ushijima [a], Hiro Matsuda [a], Toshio Fukaya [a], Fujio Mizukami [a], Jun Matsunami [b], Yuji Nagai [b] & Kazuko Matsumoto [b]

[a] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, 305, JAPAN

[b] Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo, 169, JAPAN

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NONLINEAR OPTICAL PROPERTIES OF ONE-DIMENSIONAL PLATINUM COMPLEXES

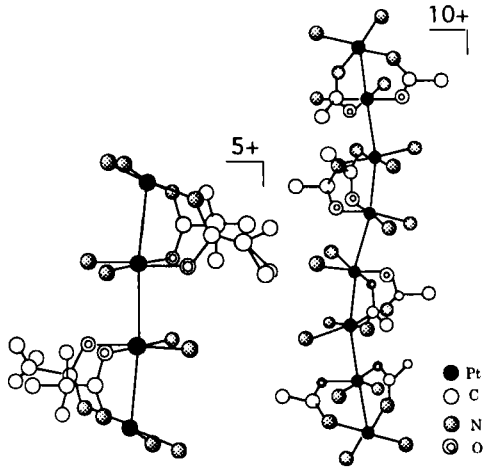
TAKEHITO KODZASA, TOSHIHIDE KAMATA, HIROBUMI USHIJIMA, HIRO MATSUDA, TOSHIO FUKAYA, FUJIO MIZUKAMI, JUN MATSUNAMI*, YUJI NAGAI*, AND KAZUKO MATSUMOTO*
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, 305, JAPAN.
*Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo, 169, JAPAN.

Abstract Third harmonic generation measurements of composite films of one-dimensional polynuclear platinum complexes with poly(vinyl alcohol) were performed. The third-order nonlinear susceptibility $\chi^{(3)}$ of the tetranuclear complex was estimated. The $\chi^{(3)}$ value of the composite film of octanuclear complex was obtained. This value is larger than that of tetranuclear complex. It indicates that the longer platinum chain leads to the enhancement of their third-order optical nonlinearity.

INTRODUCTION

Recently, a series of materials having large third-order nonlinear susceptibility $\chi^{(3)}$ generated great interest for the development of optical telecommunication. It is well known that π-conjugated organic polymers and semiconductors showed large third-order nonlinear optical effects.[1,2] It is suggested that their properties were enhanced by the excited electron delocalized in the low-dimensional quantum field. However, there is only a few investigations on the relationship between the size of low-dimensional field and third-order nonlinear optical property. We have already reported bis(dimethylglyoximato) platinum(II) having the infinite platinum chain showed large third-order nonlinear optical property.[3] Then we focused on other platinum complexes(FIGURE 1). They have finite platinum chain and delocalized electrons in

one molecule. To get reliable optical constants in the solid state, samples should be processed in such a way to obtain the transparent thin films. However, these complexes are difficult to be processed in the form of thin film by sublimation or casting from the solution. We have already prepared transparent thin films of them by using poly(vinyl alcohol)(PVA) as the matrix.[4] In this study, we have measured the $\chi^{(3)}$ value of the complex/polymer composite films. These experiments enabled us to investigate the relationships between the length of the chain for the mobile electrons and their third-order nonlinear optical properties.



(PAB) (PA8)

FIGURE 1 Molecular structure of the complex ions used in this study.

EXPERIMENTAL

The synthetic procedure and structural data of platinum complexes; $[(Pt^{2+})_3Pt^{3+}(NH_3)_8(C_5H_{10}NO)_4](CF_3SO_3)_5$ (PAB) and $[(Pt^{2+})_6(Pt^{3+})_2(NH_3)_{16}(C_2H_4NO)_8](NO_3)_{10}\cdot 4H_2O$ (PA8) have been reported elsewhere.[5,6] The composite films were obtained by casting the mixed solution of each complex and PVA in dimethyl formamide(DMF).

The optical absorption spectra of the films were recorded by a Shimadzu UV-3100 spectrophotometer. The $\chi^{(3)}$ values of composite films were estimated by the third harmonic generation(THG) Maker-fringe method. This measurement was carried out between 1.56 and 2.04μm of fundamental wavelength.

RESULTS AND DISCUSSIONS

It is well known that these platinum complexes exhibit redox behaviors. They are influenced by the pH of the solution or the existence of water and oxygen.[7] However, it is already reported they could keep their initial states during the preparation process of the thin films by using PVA/DMF system.[4] FIGURE 2(1) shows a strong band at 680nm. This is the intervalence transition band characteristic of ($Pt^{2+}{}_3Pt^{3+}$) state of this complex.[7] This spectrum indicates that PAB keeps the tetranuclear platinum chain in the composite film. FIGURE 3 shows that the absorption coefficient at 680nm is proportional to weight fraction of PAB in the film. These indicate that this complex is dispersed in the PVA thin film without any structural change.

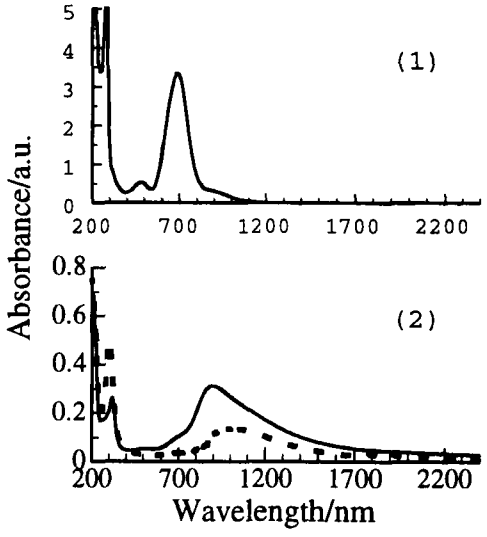


FIGURE 2 Absorption spectra of (1)PAB/PVA and (2)PA8/PVA thin films.

THG Maker-fringe measurements of composite films with different contents were performed. The $\chi^{(3)}$ value of PAB is determined by the extrapolation to a weight fraction of f=1(FIGURE 4), to be 1.2×10^{-12}esu at 2.04μm. In the same manner, $\chi^{(3)}$ values can be estimated at the various fundamental wavelength. The fundamental wavelength λ, absorption coefficient at the third harmonic wavelength α and the $\chi^{(3)}$ of PAB were summarized in TABLE I. These values are smaller than that of bis (dimethylglyoximato)platinum(II) complex(6.4×10^{-11}esu at 2.04 μm). It is expected that this difference is due to the variation of the length of platinum chain.

In FIGURE 2(2), absorption spectra of PA8/PVA composite films show a

broad band around 1000nm. Similar broad bands have been already observed in the diffuse reflectance spectrum in the solid state.[8] Therefore it indicates that PA8 keeps their octanuclear skeletal structure of platinum ions in the composite films. However, wavelength of absorption maximum depends on PA8/PVA ratio(FIGURE 5). This fact may be explained from the valence state of PA8 change in the PVA matrix.

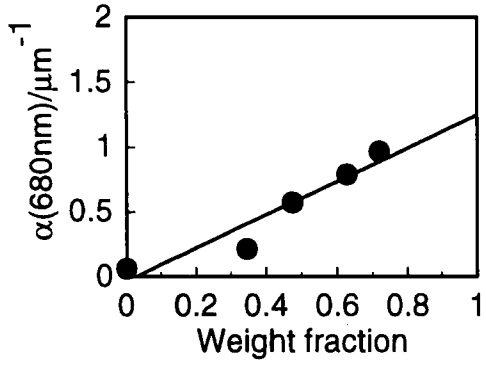


FIGURE 3 The plot of absorption coefficient of 680nm band against the weight fraction of PAB.

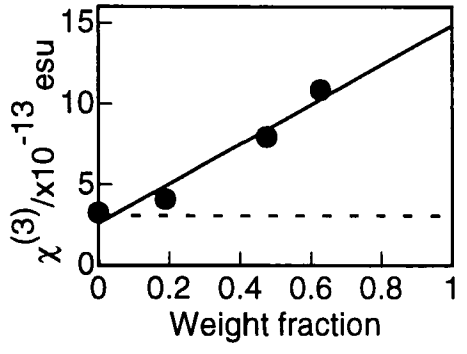


FIGURE 4 The $\chi^{(3)}$ value of PAB/PVA composite films at 2.04μm against the weight fraction of PAB.

TABLE I The absorption coefficients of third harmonic wavelength α and third-order nonlinear susceptibilities $\chi^{(3)}$ values of PAB.

λ / μm	α / cm^{-1}	$\chi^{(3)}$ / ×10^{-13}esu
2.04	12300	12
1.98	9800	7.7
1.92	8300	4.0
1.86	6330	3.6

THG Maker-fringe measurements of PA8/PVA composite thin film(weight fraction of the complex is 0.422.) are performed and is shown in FIGURE 6. 6.90×10^{-12}esu was obtained at 1.74μm of the fundamental wavelength. This value is larger than that of PAB/PVA composite film with almost same weight fraction(ab. 0.8×10^{-12}esu at 2.04μm). This results suggests that the longer conjugated platinum chain enhances the $\chi^{(3)}$ value. To clarify this point, it is required to further investigate other films with various contents of PA8.

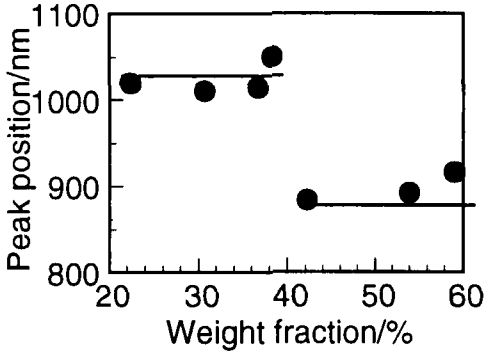


FIGURE 5 The plots of peak position of the strong absorption of PA8/PVA against the contents of PA8 in the films.

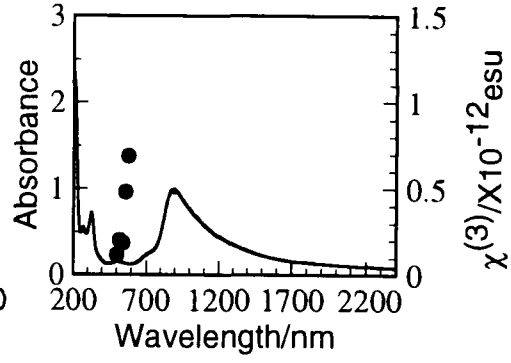


FIGURE 6 The $\chi^{(3)}$ values at the third harmonic wavelength with absorption spectrum of the composite film (42.2%g/g).

CONCLUSION

The $\chi^{(3)}$ values of the tetranuclear platinum complex PAB were obtained by the extrapolation of the value to f=1 . The largest value estimated in this study was 1.2×10^{-12} esu at 2.04μm. This value is smaller than that of bis(dimethylglyoximato)platinum (6.4×10^{-11} esu at 2.04μm), having the infinite platinum chain in the solid state. In the case of the octanuclear platinum complex PA8, the $\chi^{(3)}$ value of the composite film (weight fraction of the complex is 0.422) was 6.90×10^{-12}esu at 1.74μm. This value is higher than that of the PAB/PVA composite film with almost same weight fraction of the complex. These results indicate that the longer platinum chain leads to enhancement of their third-order optical nonlinearity.

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