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Toshio Fukaya [a] , Yuichiro Nezu [b] , Toshihide Kamata [a] & Tokiko Uchida [b]

[a] National Institute of Materials and Chemical Research

[b] Science University of Tokyo

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# MEASUREMENT OF NONLINEAR REFRACTIVE INDEX OF ONE-DIMENSIONAL METAL COMPLEXES

TOSHIO FUKAYA, YUICHIRO NEZU*, TOSHIHIDE KAMATA
and TOKIKO UCHIDA*
National Institute of Materials and Chemical Research
Science University of Tokyo*

Abstract Nonlinear refractive indexes of the dionedioximes metal complexes were measured by a surface plasmon resonance method. Extremely large nonlinear refractive index; $-1.9\times10^{-10}$ $cm^2/W$, was obtained for the $Pt(dmg)_2$ at a wavelength of 1.06μm. Index change over $10^{-3}$ was steadily realized without any defect in the sample film. The absorbance of the film at this wavelength is too small to measure. Nonlinear refractive indexes of $Ni(dmg)_2$ and $Pd(dmg)_2$ are about one order smaller than that of $Pt(dmg)_2$. These values are still very large as non-resonant regions.

## INTRODUCTION

Third-order optical nonlinearities have received much attention owing to their considerable applicability in unconventional optical devices such as all optical switching, optical logic and optical data processing.[1] Among the third-order optical nonlinear effects, the intensity dependent refractive index is a key property to realize these optical functions. The search for materials with a large nonlinear refractive index, which is a factor of changes in refractive index against light intensities, is a most important subject for the future development of optoelectronic engineering.

Since the large third-order optical nonlinearity of organic metal α-$(BEDT\text{-}TTF)_2I_3$ was reported by Huggard et. al. in 1987,[2] the nonlinear optical properties of organic metals have received great attention. Several of charge transfer complexes of metal, which have structures analogous to TTF, were shown to be good electrical conductors and have large optical nonlinearity.[3] It is said that these properties of organic metals are usually due to a partially filled conduction band formed by π orbital overlap between stacked molecules. The large optical nonlinearity in macrocycle metal complex such as porphyrins and

phtalocyanines may arise also from the extensive π electron conjugation.[4]

The $d^8$ transition metal complexes with dionedioximes have square planar form and are stacked face to face forming a linear metal chain with large *d*-orbital overlap between metals of adjointing molecules.[5] The formation of linear metal chains can be confirmed by appearance of new absorption band, which does not exist in solute samples. Energy levels of the metal-metal interactions are usually lower than those of metal-rigand interactions. They appear at visible or infrared region, which depends on the type of materials and the interval of metal chains.

We have reported formations of linear metal chains in vacuum evaporated thin films of dionedioximes metal complexes and their considerably large optical nonlinearities of third harmonic generation properties. Delocalized electrons throughout the linear metal chains and three photon resonance effects at those metal-metal absorption bands are originated to their large optical nonlinearities.[6]

The dionedioximes metal complex molecules have small regands and their molecular hyperpolarizabilities are very small compared with the macrocyclic metal complexes by one order or more. However, the bulk nonlinearities of dionedioximes metal complexes are sometimes higher than that of macrocyclic metal complexes. The $\chi^{(3)}_{THG}$ values are $10^{-12}$-$10^{-11}$esu order in each case. This type of multiplicative augmentation by assembling the metal complex molecules should be much effective than the case of the extensive π electron conjugation.

In this work we measured the nonlinear refractive indexes of the dionedioximes metal complexes at the off-resonance region using a surface plasmon resonance method.[7]

## EXPERIMENTAL

The surface plasmon resonance (SPR) is observed when the light couples with a plasmon mode at the interface of a material and a metal. The coupling angle is very sensitive to the refractive index of the material. Nonlinear refractive index of a material is determined from the intensity dependence of this coupling angle. To couple light into plasmon modes, it is necessary to make a grating in the boundary between sample and metal.[8] The SPR samples were prepared as follows. Base gratings were made by embossing poly-vinyl-chloride plates to a heated master holographic grating. A silver layer of 0.1μm was vac-

uum evaporated on the grating surface. Finally, a thin layer of dionedioxime was vacuum evaporated on to the silver surface.

According to the theory of surface plasmons,[8,9] a plasmon is excited when the following coupling condition is fulfilled:

$$\frac{\omega}{c}\sqrt{\frac{\varepsilon_a\varepsilon_b}{\varepsilon_a+\varepsilon_b}}\left(1+\frac{n_{NL}\varepsilon_a I}{\sqrt{\varepsilon_b}(\varepsilon_a+\varepsilon_b)}\right)=\left|\frac{\omega}{c}\sin\theta+\frac{2\pi m}{\Lambda}\right| \qquad (1)$$

where

$\omega$=angular frequency of laser light;

c=speed of light;

$\varepsilon_a$, $\varepsilon_b$=low-intensity values of permittivities of metal and material, respectively;

( $\varepsilon_a$=-49, at 1,064nm )[10]

I=light intensity;

$\theta$=incident angle;

$\Lambda$=grating spacing (=1$\mu$m);

m=coupling mode;

$n_{NL}$=nonlinear refractive index: $n_b = \sqrt{\varepsilon_b} + n_{NL} I$

Using a goniometer, reflectivities of the p-polarized laser light were measured by changing the incident angle. Incident light power and reflected light power were measured using pyroelectric joulemeters; gentec ED-100. The coupling of light into a plasmon mode causes a dip in the reflection curve, and by the nonlinearity of a material this coupling angle becomes intensity dependent.

## RESULTS

Nano-second Q-switched pulse $Nd^{3+}$:YAG laser with a wavelength of 1,064nm and a repetition rate of 10Hz was used. As dionedioximes; bis-(dimethyl-oximato) Platinum(II) [$Pt(dmg)_2$], $Pd(dmg)_2$ and $Ni(dmg)_2$ were examined. Fig. 1 shows the absorption spectrum of the vacuum evaporated thin films of these compounds. Thicknesses of these films are 120nm, 50nm and 110nm, respectively. Long absorption tailings beyond the infrared region come from the higher reflectivities of the sample surfaces than that of the reference

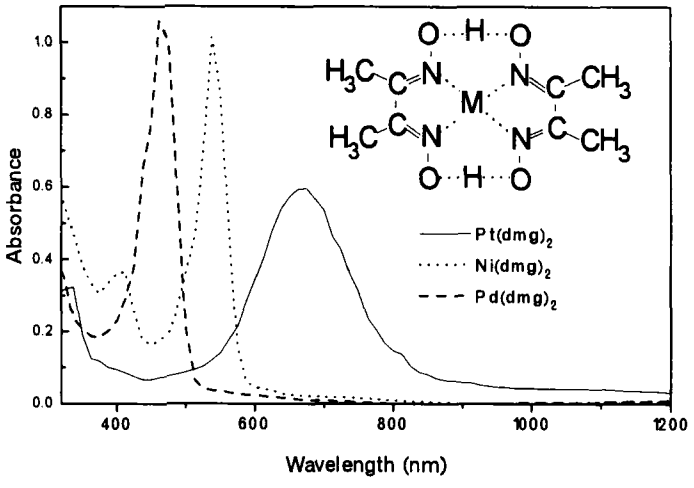


FIGURE 1 Absorption spectrum of $Pt(dmg)_2$, $Pd(dmg)_2$ and $Ni(dmg)_2$.
Long absorption tailings beyond the infrared region come from the difference of refractive indexes between the sample and the reference base glass.

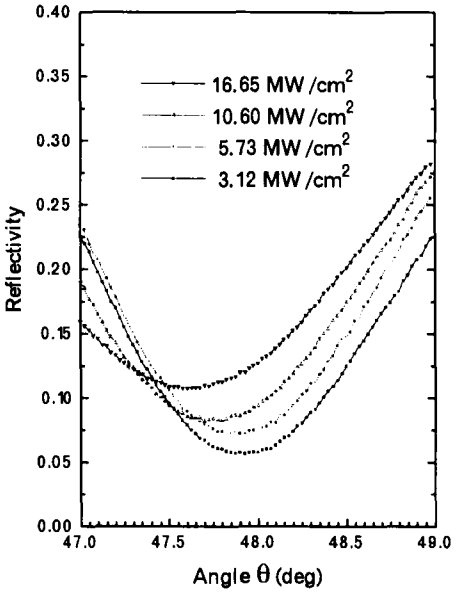


FIGURE 2 Results of goniometric measurement for $Pt(dmg)_2$. Coupling angles were shifted toward low angle when the incident intensity was increased. In this case, the nonlinear refractive index was negative.

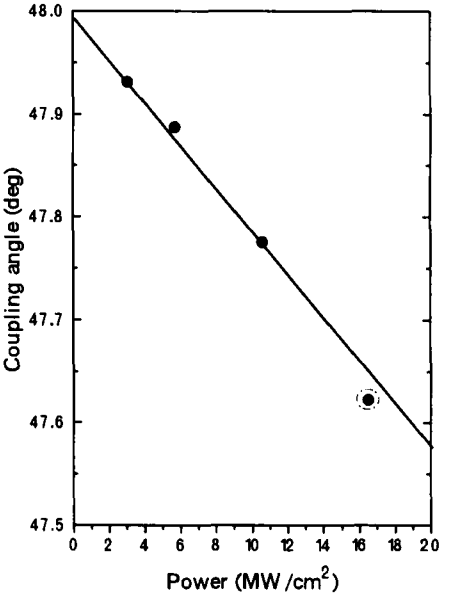


FIGURE 3 The dependence of the coupling angle on the incident power. The coupling angles were determined by analyzing the data of Fig.2 using a least squares method.
After the circled measurement, $Pt(dmg)_2$ was damaged and changed the color to white.

base glass surface. From an elipsometric measurement, refractive indexes of these samples at 1,064 nm are measured to be 1.75, 1.39 and 1.38 respectively and extinction coefficients are very small and undetectable.

We observed a dip in the reflection for various incident intensities, as shown in Fig.2. Coupling angles were determined by a least squares method and by fitting curves. From the beam profile measurement, beam diameter of 0.44mm was obtained as a full width at half maximum intensity. A pulse width of 10nsec was from a manual data. The coupling angles and the corresponding mean powers were plotted in Fig.3.

From the equation (1),

$$n_{NL} = \left(\frac{\varepsilon_a \varepsilon_b}{\varepsilon_a + \varepsilon_b}\right)^{3/2} \cos\theta \ \frac{\Delta\theta}{\Delta I} \qquad (2)^{7}$$

where $\Delta\theta=\theta_1-\theta_2$, $\Delta I=I_1-I_2$, $\theta=(\theta_1+\theta_2)/2$. The sign of the $n_{NL}$ was determined from the analysis of equation (1) by assuming our conditions and the case of first coupling mode (m=1). Before adopting this equation, the incident intensity has to be corrected by incident angle factor ($\cos\theta$). So the factor of $\cos\theta$ can be deleted from equation (2). Also corrections for reflection at air-material interface and for field enhancement at the material-Ag interface should be mentioned. The reflection and the field enhancement factor $\Gamma$ (the retio between the squares of the field amplitudes at the metal surface and in material) were calculated using plane multiple layer assumption. Total correction factor 1.9 was estimated for each samples. Thus, we determined the nonlinear refractive indexes of $Pt(dmg)_2$, $Pd(dmg)_2$ and $Ni(dmg)_2$ as $-1.94\times10^{-10}cm^2/W$, $-1.30\times10^{-11}cm^2/W$ and $-2.28\times10^{-11}cm^2/W$, respectively.

## DISCUSSION

Nonlinear refractive index of $-1.94\times10^{-10}cm^2/W$ ($\chi^{(3)}=-1.13\times10^{-8}$esu) for $Pt(dmg)_2$ is extremely very large as a non-resonant region. $Pt(dmg)_2$ changed the color to white after the dose of about ten thousands pulses at the incident power of $16.65MW/cm^2$. At least, index change of -0.002 can be steadily realized by an incident power of $10MW/cm^2$. Nonlinear refractive indexes of $Ni(dmg)_2$ and $Pd(dmg)_2$ are about one order smaller than that of $Pt(dmg)_2$. These values are still very large as non-resonant regions and their stabilities

are much higher than that of $Pt(dmg)_2$.

When the wavelength of used laser light becomes longer and apart from the absorption bands, the optical nonlinearity should be smaller. However, their optical nonlinearities at the off-resonance region are important for the situation of actual applications. It is very attractive to know how the trade-off relation between the absorbance and the optical nonlinearity will be sustained. In this paper we could not measure the $\alpha$ value of the $Pt(dmg)_2$. If $\chi^{(3)}/\alpha$ is constant for all wavelength, $\alpha<10cm^{-1}$ can be expected for $Pt(dmg)_2$ at 1,064nm. Because, $\chi^{(3)}/\alpha>10^{-9}$esu•cm was obtained at resonant region.[11]

The good processing and stability properties of the dionedioximes metal complexes increase their potential for application in integrated optics. We believe that these compounds pass the threshold for realizing the prototype optical device.

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