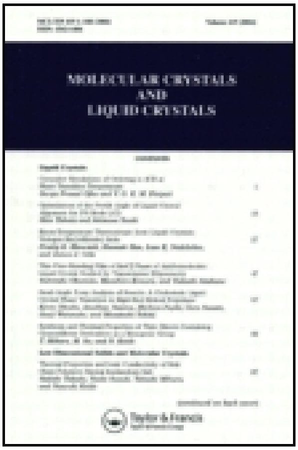

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NONLINEAR REFRACTIVE INDICES OF ONE-DIMENSIONAL METAL COMPLEXES BY Z-SCAN METHOD

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Abstract Z-scan measurements using a tunable picosecond laser were performed on one-dimensional metal complexes to investigate the nonlinear refraction and nonlinear absorption. Nonlinear refractive indices were measured to be positive/negative at wavelengths shorter/longer than the excitonic peak. Strong saturable absorption was noticeable on resonance, although small induced absorption was observed at the absorption tail. Optical nonlinearities were enhanced due to the resonance effect to give the maximum values of -8.1×10^{-7} esu and -6.7×10^{-7} esu for Re $\chi^{(3)}$ and Im $\chi^{(3)}$, respectively.

INTRODUCTION

The complexes of d^8 transition metals with dionedioxime are of great interest as third-order nonlinear optical materials. Vertically stacked molecules afford quasi one-dimensional chains of delocalized electrons along the central metals, giving large optical nonlinearities. THG and pump-probe measurements have been carried out recently for nickel, palladium, and platinum complexes, showing $\chi^{(3)}$ values as large as those of polydiacetylenes.[1-3] Tunability of the linear and the nonlinear optical properties by the appropriate choice of the metal and ligand species offers another advantage of using this series of compounds for device applications.

The nonlinear refractive index, an essential characteristic for all optical switching devices, is investigated using the z-scan technique. This simple but sensitive single-beam technique simultaneously provides the sign and magnitude of the nonlinear refractive index ($\propto \mathrm{Re}\chi^{(3)}$) and the nonlinear absorption coefficient ($\propto \mathrm{Im}\chi^{(3)}$). This work reports the z-scan results of the metal complexes at several wavelengths in the visible region.

EXPERIMENTAL

The chemical structures for metal complexes, $M(dmg)_2$ (M=Ni, Pd, Pt), are shown in Figure 1. They were synthesized according to the procedure in the previous paper,[4] and vacuum-evaporated onto fused silica glass substrates to form several hundred nanometer thick transparent films. The frequency dispersion of the refractive indices of the films was determined from Kramers-Kronig analysis using the value at 633 nm measured by the ellipsometry with a Shimadzu DE-10A ellipsometer.

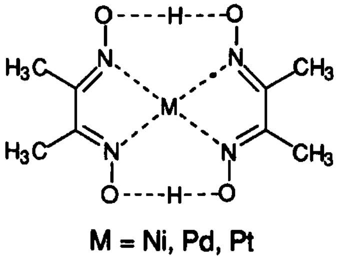

FIGURE 1 Chemical structure of $M(dmg)_2$.

A standard z-scan setup was used, in which an LBO-based OPG/OPA output (420~1800 nm) pumped by the third -harmonic from a Nd:YAG laser was employed as a light source. The pulse width was ~20 ps and the repetition rate was 5 Hz. The Gaussian beam, which is critical for the z-scan measurement, was extracted from OPG/OPA output using a spatial filter in an evacuated chamber, and the spatial profile was verified by the laser beam profiler Hamamatsu LEPAS-10. Transmittance of the sample with and without a finite aperture in the far field was recorded as the sample was scanned through the focal plane along the propagation direction z. At each z position, 10 to 15 laser shots were averaged in order to improve the signal to noise ratio. The nonlinear refractive index (γ; $n=n_0+\gamma I$) and the nonlinear absorption coefficient (β; $\alpha=\alpha_0+\beta I$) were determined from the z-scan signals using the procedure developed by Sheik-Bahae *et al.*[5] The real and imaginary parts of $\chi^{(3)}$ were calculated through the relations Re $\chi^{(3)}(esu)=(cn_0^2/16\pi^2)\gamma(cgs)$ and Im $\chi^{(3)}(esu)=(c^2n_0^2/32\pi^2\omega)\beta(cgs)$.

RESULTS AND DISCUSSION

A z-scan measurement on CS_2, carried out at 532 nm to check the experimental setup, yielded $Re\chi^{(3)}=6.0x10^{-12}$ esu. A typical z-scan signal for the metal complexes is depicted in Figure 2, and the results are summarized in Figures 3-5. The values obtained are significantly lower than those by the pump-probe measurements especially in the resonance region, *e.g.*, $Im\chi^{(3)}$(z-scan)$=-3.5x10^{-8}$ esu and $Im\chi^{(3)}$(p-p)$=-1.5x10^{-5}$ esu at

532 nm for Ni(dmg)$_2$.[2,3] However, because of the long decay time of the excited states, 1.5 to 2 ns in the above case, the earlier pump-probe $\chi^{(3)}$ values were analyzed as effective cw-values, i.e. the $\chi^{(3)}$ values that would be measured if the pulse widths were much longer than the decay time. This extrapolation to the cw-value is not done in the z-scan analysis.

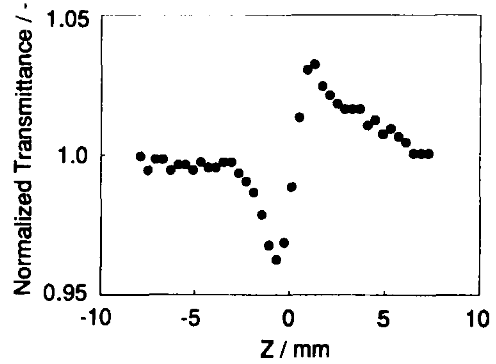

FIGURE 2 Typical closed-aperture z-scan signal for the metal complexes. [Pt(dmg)$_2$, λ=600 nm, $I_{0,\mathrm{peak}}$=0.21 GW/cm^2]

The three figures have common spectral features. First, more than two orders of magnitude enhancement is achieved for Re$\chi^{(3)}$ and Im$\chi^{(3)}$ by the resonance effect. Second, there exists a crossover of the sign of Re$\chi^{(3)}$ at the excitonic peak from negative at longer wavelengths to positive at shorter wavelengths. Third, both the saturable absorption (- Im$\chi^{(3)}$) and induced absorption (+ Im$\chi^{(3)}$) are observable across the crossover point sitting on the absorption tail, although the latter is much smaller in magnitude. This is similar to the results of pump-probe measurement. In this study, the complex with the lowest energy excitonic peak, Pt(dmg)$_2$, also had the largest values of Re$\chi^{(3)}$ and Im$\chi^{(3)}$: -8.1x10^{-7} esu and -6.7x10^{-7} esu, respectively.

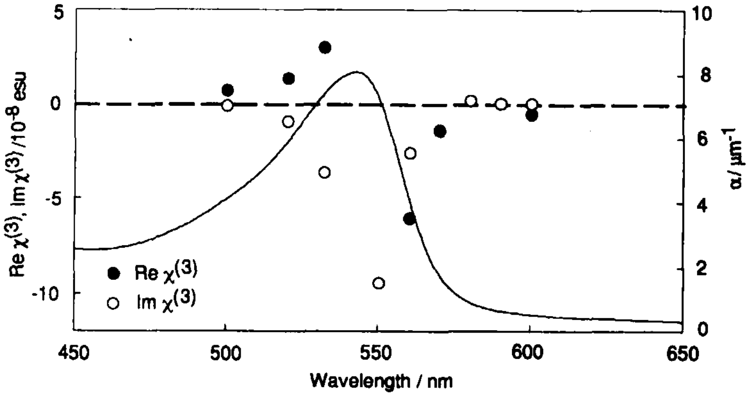

FIGURE 3 Wavelength dependence of Re $\chi^{(3)}$ and Im $\chi^{(3)}$ for Ni(dmg)$_2$. Also shown is the linear absorption spectrum.

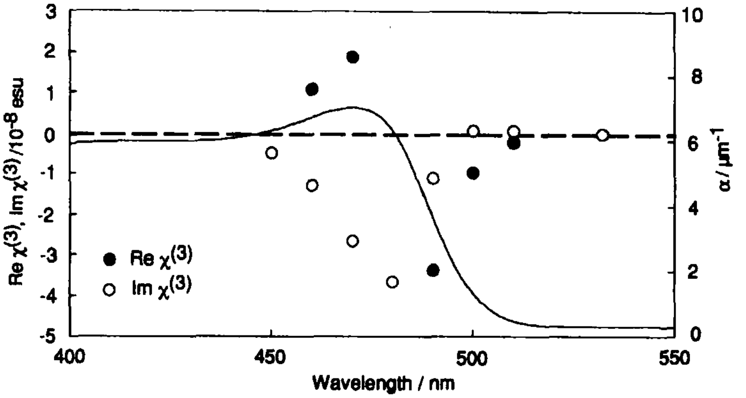

FIGURE 4 Wavelength dependence of Re $\chi^{(3)}$ and Im $\chi^{(3)}$ for Pd(dmg)$_2$. Also shown is the linear absorption spectrum.

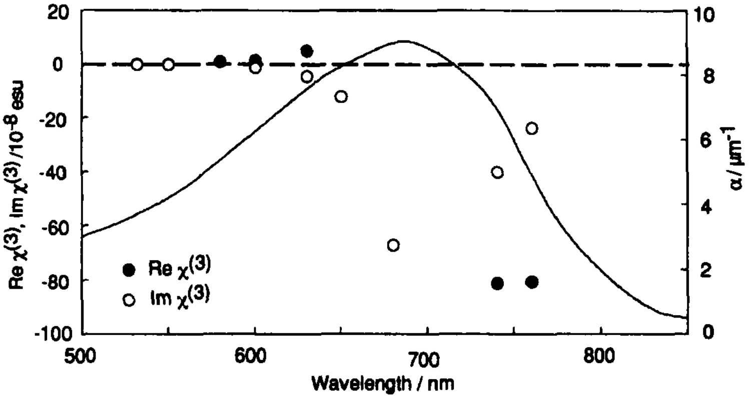

FIGURE 5 Wavelength dependence of Re $\chi^{(3)}$ and Im $\chi^{(3)}$ for Pt(dmg)$_2$. Also shown is the linear absorption spectrum.

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