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X(3)of M-X Chains

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Abstract The third-order nonlinear optical susceptibility has been investigated for oriented thin films of halogen bridged platinum complexes. The $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ spectrum associated with the third harmonic generation (THG) was measured by the Maker fringe method in the region of fundamental wavelength $0.6\mu m \sim 1\mu m$ and $1.6\mu m \sim 2.2\mu m$. In the $|\chi^{(3)}|$ spectra, we found a peak structure at $\omega \sim 1.8$eV that is attributable to a two-photon resonance to the optically forbidden charge transfer exciton. The $|\chi^{(3)}|$ value was in the order of 10^{-11}esu that is comparable to the π-conjugated polymers. Common features of NLO processes for the one-dimensional semiconductors are discussed.

Introduction

Nonlinear optical (NLO) properties of conjugated polymers are attracting much attention due to their large NLO susceptibilities and ultrafast response. Recent studies reveal that the precise determination of the one-dimensional (1D) electronic structures is indispensable to understand the NLO processes[1]. One of the experimental approach to get such information is to explore a new generation of 1D semiconductors and to make various kinds of NLO spectroscopy.

From this point of view, the halogen bridged mixed valence

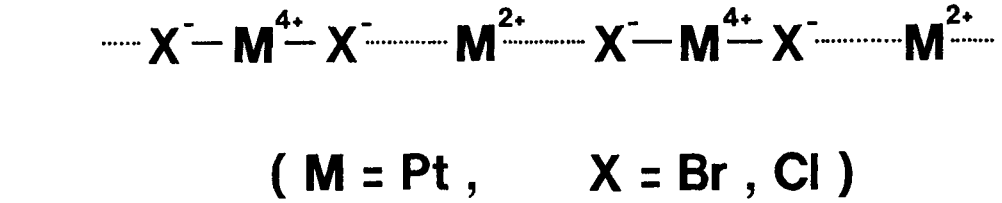

Figure 1 Schematic 1D structure of M-X chain compounds.

complexes, so called M-X chain compounds, are of great interest, since they are known to be ideal 1D semiconductors[2]. Here, M and X represent transition metals and halogens, respectively. A linear chain structure of this compound is schematically shown in Fig.1. Among various kinds of M-X chain compounds, we have chosen the most popular group which are represented by the following formula.

$$[MA_2]\ [MA_2X_2]\ Y_4 \qquad (1)$$

Here, A stands for a ligand molecule and Y for a counter anion. As seen in Fig.1, the position of halogen ions are slightly shifted from the midpoint of metal ions. This causes a disproportionation of the metal ions as depicted in the formula (1). The alternate structure of M^{2+} and M^{4+} or the mixed valent state can be regarded as a charge density wave state similar to polyacetylene[3]. The Peierls gap of 1~3 eV can be controlled by changing metal (M=Pt, Pd, Ni), halogen (X=Cl. Br, I), and other elements.

The lowest electronic transition is assigned to a charge transfer (CT) exciton from M^{2+} to neighboring M^{4+}. According to the work by Wada et al.[4] on Pt complexes, the oscillator strength of the CT band is extraordinarily large (f=3~6 as defined for the 'MXMX' unit), possibly due to the one-dimensional nature of the CT exciton. They also insist that the CT exciton state is extended to several sites along the M-X chain. The large oscillator strength and extended wave-function of CT excitons are favorable for the enhancement of optical nonlinearity of this compound.

Experimental results

We have applied the third harmonic generation (THG) method, which are popular for conjugated polymers[1]. For this purpose we have fabricated oriented thin films of $[Pt(en)_2][Pt(en)_2X_2](ClO_4)_4$ (X=Cl, Br). In the formula (1), A=en(ethylenediamine) and $Y=ClO_4$. These substances are hereafter abbreviated as Pt-Cl and Pt-Br. The method of fabricating thin films are shown in the previous paper[5]. Typical polarized absorption spectra of Pt-Cl and Pt-Br are shown in Fig.2. The optical density ratio between the parallel and perpendicular components to the M-X chain axis are 9 and 100 for Pt-Cl and Pt-Br, respectively. A high degree of orientation is guaranteed by this large optical anisotropy.

Asymmetric spectral shape is in good agreement with the ε_2 spectra of the Pt-Cl and Pt-Br single crystal[4]. Three kinds of light source were utilized for the THG measurements. The fundamental beam of 2.2μm~1.6μm was obtained by a difference-frequency generation between a Q-switched Nd:YAG laser and a tunable dye laser. From 0.82μm to 0.58μm, we used a tunable dye laser driven by a Xe-Cl excimer laser. For 1.06μm, a Q-switched Nd:YAG laser was used. The pulse duration of these lasers were 5~15ns, and the power density was kept less than several tens of MW/cm^2. We successfully observed the TH light from the Pt-Cl film, however the measurement on Pt-Br was unsuccessful due to the low threshold of degradation by the laser pulse.

Figure 3 shows Maker fringe patterns of the standard silica plate and the Pt-Cl film for the fundamental photon energy at 2.02eV. From this figure, we obtain the TH intensities I and I_S from the sample film and silica plate, respectively. Using these quantities, we evaluated the $|\chi^{(3)}|$ value from the following equation.

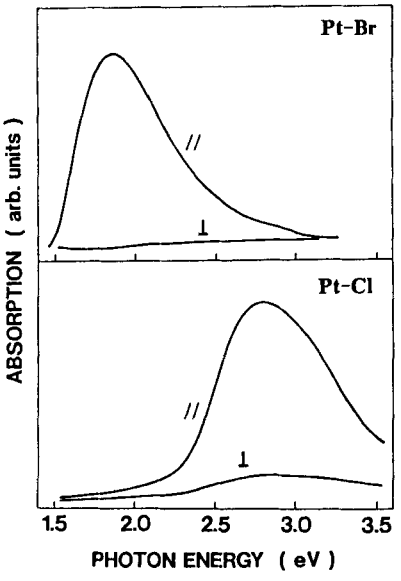

Figure 2

Polarized absorption spectra of Pt-Br (upper part) and Pt-Cl (lower part) oriented thin films.

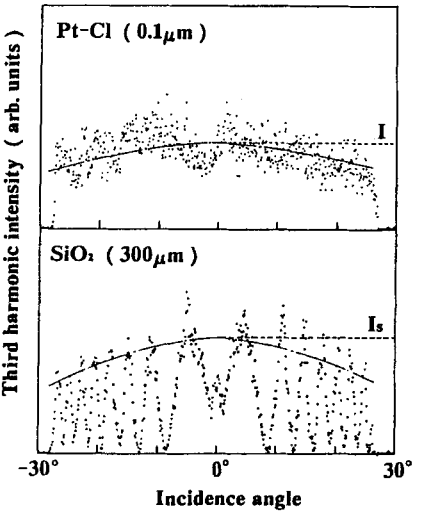

Figure 3

Maker fringe pattern of the Pt-Cl film (upper part) and the silica plate (lower part) for the fundamental photon energy of 2.02eV.

$$|\chi^{(3)}| = \frac{2}{\pi} \cdot \sqrt{\frac{I}{I_s}} \cdot \frac{l_{c,s}}{l} \cdot |\chi_s^{(3)}| \qquad (2)$$

Here, $l_{c,s}$, $|\chi^{(3)}_s|$ are the coherence length and the third-order NLO susceptibility of silica, respectively. The $|\chi^{(3)}_s|$ was calculated using the empirical Miller's rule and the $l_{c,s}$ was estimated from the dispersion of the refractive index of silica. The energy dependence of these quantities are shown in this issue[6].

In Fig.4, the $|\chi^{(3)}|$ values are plotted as a function of fundamental photon energy ω for Pt-Cl. The incident laser was polarized parallel to the chain axis. The perpendicular component was about one-order of magnitude smaller than the parallel one. The most important result is that the $|\chi^{(3)}|$ values of Pt-Cl were found to be in the order of 10^{-11} esu. This value is comparable to that of π-conjugated polymers[7] or even larger than that of σ-conjugated polymers polysilanes[6].

It is also noted that the $|\chi^{(3)}|$ spectrum shows a peak structure at about 1.8eV. This peak provides a useful information to deduce a

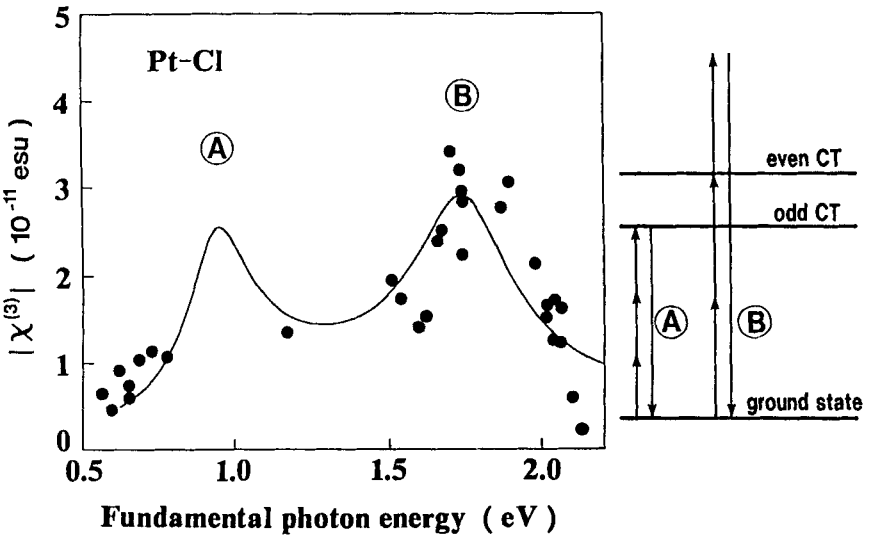

Figure 4

$|\chi^{(3)}(-3\omega;\ \omega,\omega,\omega)|$ spectrum for the Pt-Cl film as a function of fundamental photon energy ω (solid circle). A calculated $|\chi^{(3)}|$ spectrum using the equation (3) is plotted by a thin solid line in arbitrary units. The energy diagram for Pt-Cl and THG processes are also shown on the right side.

microscopic mechanism of NLO processes in M-X chains. The peak in the $|\chi^{(3)}|$ spectrum can be explained neither by the three-photon resonance nor by the two-photon resonance to the CT exciton at 2.8eV. We attribute the 1.8eV peak to the two-photon resonance to the one-photon forbidden CT exciton which is found by the electromodulation spectroscopy.

Discussion

According to Wada et al.[8], the excited states of M-X chain compounds are formed of two CT excitons. One is the one-photon allowed CT exciton with an odd symmetry. The absorption spectra in Fig.2 are attributed to this odd CT exciton. The other one is the one-photon forbidden CT exciton with an even symmetry. This exciton is observed as a field-induced absorption in the electroabsorption spectra. The energy of the even CT exciton is slightly larger than that of the odd CT exciton. Therefore, the energy diagram for Pt-Cl is obtained as shown on the right of Fig.4.

Based on this three-level model, we calculated the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ spectra. The leading term of the THG process is shown in the following equation.

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) \propto \frac{f_{go} \cdot f_{oe}}{(\omega_o - 3\omega - i\Gamma_o)(\omega_e - 2\omega - i\Gamma_e)(\omega_o - \omega - i\Gamma_o)} \quad (3)$$

Here, f_{go} is the oscillator strength between the ground state and odd CT exciton, and f_{oe} is that between the odd and even CT excitons. ω_o=2.8eV and ω_e=3.5eV are the energies of the odd and even CT excitons that are obtained from the electroabsorption spectra at room temperature[5]. The Γ_o and Γ_e are the damping factors of the odd and even CT excitons, respectively. The calculated $|\chi^{(3)}|$ spectrum is shown in the thin solid line in Fig.4. The quantities of Γ_o and Γ_e are assumed to be 0.3eV. Due to the ambiguity of parameters such as local field factors or the damping factors, the calculated spectrum is shown in arbitrary units. The experimentally found peak at about 1.8eV is qualitatively explained by the B peak in the calculated spectrum. As shown in the energy diagram in Fig.4, the B structure is understood in terms of a two-photon resonance to the even CT exciton. These results directly indicates that the one-photon forbidden state plays a

crucial role in the THG process in the Pt-Cl compound. The calculation predicts another peak structure A, which are attributed to the three-photon resonance to the odd CT exciton. Further measurements are being undertaken to obtain full $|\chi^{(3)}|$ spectra that possibly give us more valuable information.

It should be stressed here that the energy diagram in Fig.4 is quite useful to explain the $|\chi^{(3)}|$ spectra of other 1D semiconductors such as π- or σ-conjugated polymers[9]. In the case of polymeric materials, the one-photon allowed state corresponding to the odd CT exciton is called ^1B_u. The one-photon forbidden state is called ^1A_g. One may expect that the two-photon resonance in the $|\chi^{(3)}|$ spectra similar to that in Fig.4 should be observed also in the polymeric materials. It was really found in polyacetylene by Kajzar et al.[10], and recently in polysilanes[6]. These facts prove the similarity of electronic structure between M-X chain compounds and conjugated polymers. One of the most simple physical picture for the excited states in polymers is the 1D Wannier exciton model[11]. In the M-X chain compounds, on the other hand, the excitons have a strong charge transfer character. Even though the exciton characters are different, the energy structures of the excited states related to the NLO processes are common to various kinds of 1D semiconductors.

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