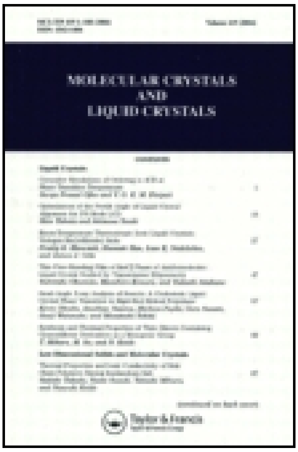

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ULTRAFAST OPTICAL RESPONSE IN QUASI-ONE DIMENSIONAL HALOGEN-BRIDGED MIXED-VALENCE COMPLEXES $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$ AND $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$

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Abstract Ultrafast optical response in two quasi-one-dimensional halogen-bridged mixed-valence complexs $[Pt(en)_2][PtBr_2(en)_2]$ $(ClO_4)_4$ (en=ethylenediamine) (abbreviated as PtBr) and $[Pd(en)_2][PdCl_2(en)_2]$ $(ClO_4)_4$ (as PdCl) has been investigated by femtosecond absorption spectroscopy at room temperature by pump-probe spectroscopy. The photo-induced absorption around 1.3 eV and the bleaching from 1.5 eV to 2.7 eV were observed in PtBr. Both consist of a fast-decay component due to STEs and a slow-decay component due probably to polaron pairs. The former decays exponentially with the time constant of 1.4 ± 0.2 ps. The latter decays as $\mathrm{erf}(t^{\beta})$ with $\beta = -0.22 \pm 0.02$, indicating the geminate recombination of an electron polaron and a hole polaron after moving freely along the chain. The deviation of β from the ideal random-walk model ($\beta = -0.5$) is explained by introducing the effect of potential barrier between the polarons hindering the recombination. A pump-probe absorption spectrum of PdCl is obtained from the reflection spectrum by the Kramers-Kronig relations. The time dependence of the transient photoinduced absorption around 1.7 eV and the bleaching from 1.9 eV to 2.5 eV were calculated to be described with three components. They correspond to free excitons with lifetime of about 800 fs, self-trapped excitons with lifetime of about 3 ps, and polaron pairs which hardly relax within 100 ps.

INTRODUCTION

Quasi-one-dimensional halogen-bridged mixed-valence complexes, or MX chains in short, are the typical examples showing the charge density wave CDW state, and are useful for studies of their photo-excited states and their relaxation processes as one-dimensional electron systems [1]. The strong electron-phonon interaction is very important in one-dimensional systems for their ultrafast optical nonlinear response, and such low dimensional systems are attracting scientists in various fields [2-4]. MX chains have a structure consisting of linear chains of alternating transition-metal (*M*) ions and halogen (*X*) ions.

$$-M^{(3+\delta)+}-X^{-}---M^{(3-\delta)+}---X^{-}-M^{(3+\delta)+}-X^{-}---M^{(3-\delta)+}- - -,$$

where $\delta(0 \leq \delta \leq 1))$ stands for the deviation of the valency from 3. MX chains have an intense broad absorption band (CT band) polarized along the chain axis in the visible region due to the charge transfer transition over the CDW energy gap [5-7]. Luminescence from the self-trapped state with a Stokes shift, which is as large as a half of the gap was found[6,8], indicating that the electron-phonon interaction is strong in these materials. Kurita *et al.* [9,10] have found that two long-lived photo-induced absorption bands of $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ appear at 77 K. These bands were attributed to polarons created in pairs by photo-excitation from the data of photo-induced electron-spin resonance [10], halogen doping [11], and theoretical researches [12-14]. Compared with conjugated polymers [15], time-resolved measurements have not been made for MX chains except a few [16,17], even though these materials are of interest because of their characteristic features and of being another prototype for studying quasi-one-dimensional systems. The lifetime of the luminescence of STEs (self-trapped excitons) is of the order of 100 ps at low temperature, and decreases as temperature increases [16,17]. However, the luminescence measurement is only limited to the materials with the large CT gap (about 3 eV) at low temperature, otherwise the efficiency of luminescence is extremely low and time-resolved measurement is not possible.

In this paper, we report for the first time the femtosecond time-resolved absorption spectra of such a mixed-valence compound using $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$ and $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$, abbreviated as PtBr and PdCl respectively, as samples in the femtosecond time range by the pump-probe spectroscopy. The experiment is expected to offer the direct clues for clarifying the relaxation processes of MX chains from their photo-excited states.

RESULTS AND DISCUSSION

PtBr

The time-resolved spectra of the photo-induced absorption change in a thin film of PtBr at room temperature up to 100 ps after photo-excitation are shown in Fig.1. The stationary absorption spectrum of PtBr with linearly polarized light at room temperature is shown at the top. The data around the excitation energy are not shown, because of the disturbance due to scattering of the excitation light.

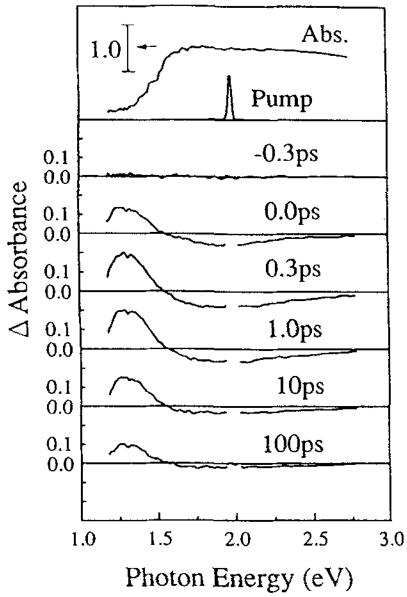

FIGURE 1. The photo-induced differential absorption spectra of PtBr at room temperature up to 100 ps after photo-excitation at 1.99 eV. Pulse duration and photon density of the excitation are 100 fs and 7.4 x 10^{15} photons/cm^2, respectively, and the pump and probe pulse are both polarized along the chain. The absorption spectrum (Abs.) and the pump laser spectrum (pump) are also shown at the top.

Since photo-induced absorption around 1.3 eV and bleaching from 1.6 eV to 2.7 eV are observed only for the excitation light polarized parallel to the chain, they are due to the CT excitation.

The following function was used for fitting the time dependence of the photo-induced absorbance changes ΔA

$$\Delta A(t) = A_1\cdot\exp(-t/\tau_1) + A_2\cdot\mathrm{erf}((t/\tau_2)^{\beta}). \quad (1)$$

The fitting was performed by the convolution of Eq.(1) with the pump and probe pulse profiles, which were assumed as Gaussian type. The parameters τ_1, τ_2, and β are determined as 1.4± 0.2 ps, 10± 4 ps and -0.22±0.02, respectively at several photon energies including 1.35 eV and 2.03 eV. The first term and second are attributed to STEs and polaron pairs respectively. the latter assignment is firstly because the peak position around 1.3 eV of the photo-induced absorption band observed is close to that of the polaron band observed by Okamoto *et al.*[18] Secondly, the temporal behavior of the long-lived component proportional to t^{β} indicates that this process is due to the recombination of pair species[19]. An electron polaron (P^-) and a hole polaron (P^+) are generated in pairs by photo-excitation, move freely along the MX chain, and recombine geminately by the collision. The polaron band around 1.3 eV in Fig.1 seems to consist of two peaks. Most probable interpretation is that one peak is due to electron polarons and the other to hole polarons as shown by Gammel *et al.*[20]

There is another possibility of the assignment of the slow component, i.e., soliton pairs. Further study is needed to identify the transient absorption.

The value of β in the ideal case of random walk in one dimensional system is expected to be -0.5, but the absolute value obtained in this experiment is smaller.The deviation of β from the ideal random-walk model (β = -0.5) is explained by introducing the effect of potential barrier between the polarons hindering the recombination.

The excitation intensity dependence of the amplitude of two components, namely A_1 and A_2 in Eq.(1), in the energy range of photo-induced absorption is shown in Fig.2. The integrated absorbance change of probe photon energy from 1.25 eV to 1.40 eV is used as ΔA. Apparently, A_1 and A_2 show the different dependence on the excitation intensity.

If it is assumed that STEs and polaron pairs originate from the same FE states, the absorbance due to the fast decay component $A_1(I)$ and that due to slow decay component $A_2(I)$ should have the same I dependence, because saturations in $A_1(I)$ and $A_2(I)$ are most probably due to the saturation of the FE states. Therefore it can be considered that STEs and polaron pairs originate from the different states of FE as predicted by Mishima and Nasu[12]. Another possible reason for the difference between A_1 and A_2 is that the slow-decay component(A_2) may be attributed to two kinds of polarons. One is the polarons generated by one photon, and the other is generated by two photons or two-step excitation. Two-step excitation means the process that FEs generated by one photon are excited again by another photon to higher states before relaxation. Even though the component due to one-photon excitation shows similar tendency to the fast-decay component (A_1), the component due to two-photon excitation or two-step excitation would have different dependence. As a result, A_2 is expected to be nearly proportional to the excitation intensity.

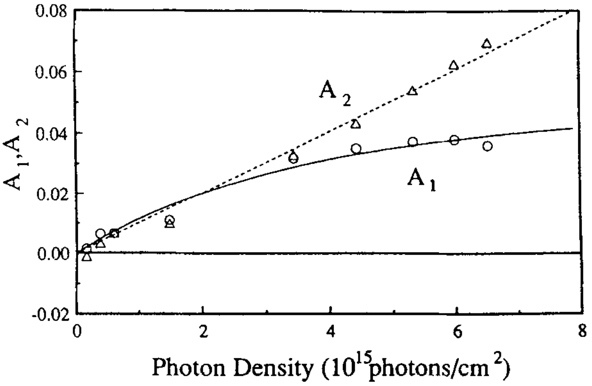

FIGURE 2 The excitation intensity dependence of the amplitude of two components, A_1 and A_2 in Eq.(1), in the energy range of photo-induced absorption. The integrated absorbance change of probe photon energy from 1.25 eV to 1.40 eV is used as ΔA. Open circles and triangles represent the experimental data for A_1 and A_2, respectively. The solid curve and broken straight line represent the result of fitting A_1 and A_2, respectively.

PdCl

PdCl has a strong reflection band with a peak around 2.2 eV with parallel polarized light to the chain of the sample[7]. It is due to the CT exciton transition. The time-resolved spectra of the photoinduced reflection change in PdCl at room temperature up to 100 ps after photoexcitation are shown in Fig.3. The excitation photon energy of 1.97 eV is resonant with the exciton absorption. The pulse duration and photon density of the excitation are about 100 fs and 3.6 x 10^{15} photons/cm^2, respectively. The pump and probe are both polarized parallel to the chain of the sample. Fig.4 shows the absorption difference spectra obtained with the Kramers-Kronig relations.

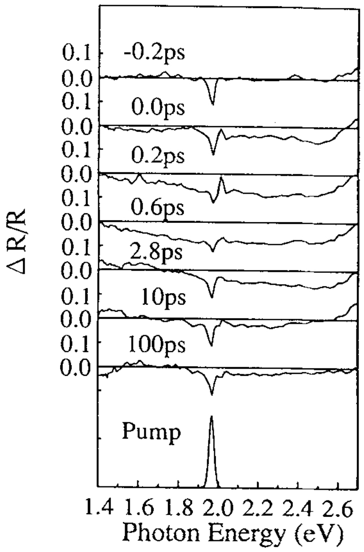

FIGURE 3 The photoinduced differential reflection spectra in PdCl at room temperature up to 100 ps after photoexcitation at 1.97 eV. Pulse duration and photon density of the excitation are 100 fs and 3.6 x 10^{15} photons/cm^2, respectively, and the pump and probe pulse are both polarized along the chain. The pump laser spectrum (pump) is also shown at the bottom.

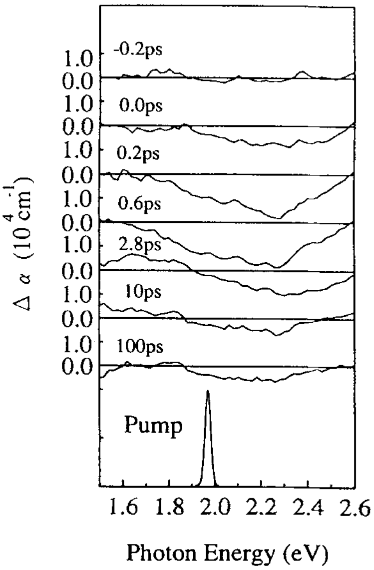

FIGURE 4 The photoinduced difference spectra in absorption coefficient in PdCl obtained by applying Kramers-Kronig relation to the reflection data in Fig.3.

The time dependence of the photoinduced changes in absorbance is expressed as a constant in the following function to fit the data:

$$\Delta\alpha(t) = A_1\cdot\exp(-t/\tau_1) + A_2\cdot\exp(t/\tau_2) + C \qquad (2)$$

A pump-probe absorption spectrum of PdCl is obtained from the reflection spectrum by the Kramers-Kronig relations. The time dependence of the transient photoinduced absorption around 1.7 eV and the bleaching from 1.9 eV to 2.5 eV were calculated to be described with three components. They correspond to free excitons with lifetime of about 800 fs, self-trapped excitons with lifetime of about 3 ps, and polaron pairs which hardly relax within 100 ps.

CONCLUSION

For the case of sample PtBr, the photo-induced absorption around 1.3 eV and the bleaching from 1.5 eV to 2.7 eV were observed, and both consist of two components. One is the fast-decay component which maybe is due to STEs with the lifetime about 1.4 ps, and the other is the slow-decay component due to polaron pairs. For the case of sample PdCl, the reflection spectra are transformed into the absorption ones by the Kramers-Kronig relations. The temporary photoinduced absorption around 1.7 eV and the bleaching from 1.9 eV to 2.5 eV were observed, and the decay profile is expressed by about 800 fs, 3ps, and > 100ps components which is considered to correspond to the FE states, STE states, and the polaron pairs, respectively.

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