Ultrafast Photoluminescence Dynamics in a Quasi-one-dimensional Halogen-bridged Mixed-valence Complex $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$

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Ultrafast dynamics of luminescence from the unrelaxed self-trapped excitons in a quasi-one-dimensional halogen-bridged mixed-valence complex $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (en = ethylenediamine) has been investigated for the first time by femtosecond up-conversion method. The photoluminescence lifetime increases from 270 fs to 1.2 ps with wavelength from 570 nm to 660 nm. At longer wavelengths than 660 nm a component with a much longer lifetime than 10 ps was also observed.

Spectroscopies of halogen-bridged mixed valence complexes (hereafter abbreviated as MX-chain) have been studied actively [1-4] from the viewpoints of peculiarity of the dimensionality and geometrical relaxation induced by the strong vibronic (electron-phonon) coupling.[5] The study of the ultrafast dynamics in the time range of femtosecond is very important to clarify the relevance of the coupling to the extremely large Stokes shift in the complexes.[1-4] In a MX-chain complex, metal (M = Pt, Pd, and Ni) and halogen (X = Cl, Br, and I) ions form a one-dimensional chain. The metal ions are surrounded by various ligand molecules such as ethylenediamine (en). The complexes containing Pt or Pd are the one-dimensional systems in which the halogen distortions from the central positions of the two nearest neighboring metal ions cause the charge-density waves (CDWs) with a doubled period of the metal to metal distance.[6] Phase boundaries in the double period between the neighboring two phases reversed domain are either solitons or polarons. Similar nonlinear excitation can be photogenerated in a conjugated polymer with a degenerate ground state namely *trans*-polyacetylene.[7-9]

Stationary photoluminescence from the MX mixed-valence complex has commonly large Stokes shift which is attributed to the geometrical relaxation taking place after photoexcitation.[10, 11] The time required for the geometrical relaxation induced by the vibronic (electron-phonon) coupling in a conjugated polymers with the degenerate ground state was theoretically predicted to be of the order of 10^{-13} s.[7-9] Shank and others measured the absorption of the soliton pair in trans-polyacetylene photogenerated by a femtosecond laser and the formation time could not be resolved.[12] In our previous papers, we could resolve the formation of the soliton pairs for the first time in three substituted polyacetylenes for the first time to be between 50 and 100 fs depending on the substituent group.[13,14] The primary processes were also studied in two MX complexes by femtosecond pump-probe spectroscopy, but the formation of the soliton pair could not be resolved.[15, 16] In the present paper we for the first time have observed the fluorescence from nonequibrium self-trapped exciton state before full geometrical relaxation in a MX complex.

The fluorescence decay in the femtosecond region was measured using a femtosecond fluorescence up-conversion system.[17] A fundamental titanium (Ti):sapphire laser at 807 nm (1.54 eV) with an average power of 600 mW and a repetition rate of 100 MHz was used to produce the second harmonics (SH) at 403.5 nm (3.07 eV) with an average power of 10 mW in a 3-mm LBO crystal (type I). The SH of 1 mW average power was used to excite the samples. The cross correlation between the SH and the fundamental for up-conversion had a full width at half-maximum of 260 fs when an objective lens was used for collecting the fluorescence.

Figure 1 shows the time dependence of the fluorescence intensity from the PtCl sample excited at 403.5 nm probed at four different wavelength 570, 600, 630, and 660 nm, corresponding photon energies 2.18, 2.07, 1.97, and 1.89 eV, respectively. Three photon energies were selected for the study of ultrafast relaxation just below the absorption spectrum. In the spectral region emission with ultrashort lifetime is expected because of ultrafast geometrical relaxation in one-dimensional system is taking place. All the intensities of the stationary fluorescence at the photon energies of 2.18, 2.07, 1.97, and 1.89 eV are about

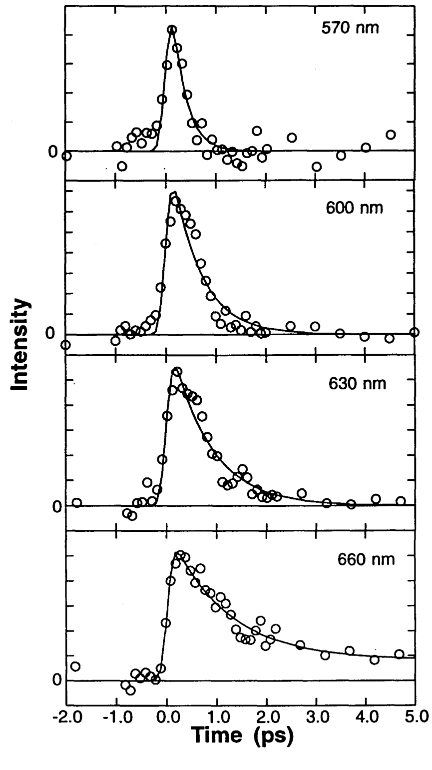

Figure 1. Time dependence of fluorescence intensity from $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ measured by up-conversion method at room temperature.

1.5 x 10^{-3}, 1.6 x 10^{-3}, 1.8 x 10^{-3}, and 2.0 x 10^{-3} of that at the peak near 1.2 eV. Because of this weak intensity the signal obtained by femtosecond up-conversion method has a small signal to noise ratio. The decay at 570, 600, and 630 nm can be fitted with a single-exponential function while that at 660 nm is fitted with an exponential function plus a component with much longer lifetime than 10 ps. The latter is set at constant. The time constants of the exponential functions are 270 fs, 580 fs, 780 fs, and 1.2 ps at 570, 600, 630, and 660 nm, respectively. The contribution of the Raman signal to the shortest time at 570 nm can be safely eliminated because of the following reason. The largest Stokes Raman shift of the highest overtone observed by Tanino and Kobayashi[2] is the 17th of the metal-halogen stretching vibrational mode with the frequency of 316 cm^{-1}. The Stokes Raman shifted from the SH of the Ti:sapphire laser by 5372 (=316×17) cm^{-1} is expected to appear around 20000 cm^{-1} corresponding to 500 nm. Therefore, the wavelength is much shorter than any of the fluorescence probe wavelengths for the decay time measurement in the present experiment and the Raman does not contribute to the fluorescence signal intensity.

The lifetime is between 70 ps and 250 ps measured previously[18] at probe photon energy between 1.34 eV. It increases with decrease in temperature and it becomes as long as 230 ps at 2K. If we neglect the inhomogeneous broadening of the absorption spectrum and also that of fluorescence spectrum, the radiative lifetime is expected to be common for all the vibrational levels. Hence the fluorescence is taking place during the geometric relaxation from the free exciton generated by 3.07 eV photon to the self-trapped exciton. The observe lifetimes are corresponding to the phonon emission process associated with the geometrical relaxation. Therefore, the fluorescence intensities are expected to be proportional to the lifetime. Using the intensities at the probed photon energies and the lifetime of 70 ps measured at room temperature by Wada et al.,[18] the estimated lifetimes at 2.18, 2.07, 1.97, and 1.89 eV are 105, 112, 126, and 140 fs, respectively. The lifetimes are much shorter than the above mentioned values directly measured especially at longer wavelengths. There are possibly two reasons of relatively large discrepancies between the observed and the estimated lifetimes. One possibility is large errors in the estimation of the relative intensities between those in the 570-660 nm region and that at the luminescence peak, but the relative valence among the formers are reliable. The other possible explanation is that the Frank-Cordon factors are different among those observed wavelength. If the system is assumed to be composed of multi-vibronic levels in which cascading phonon emission is taking place in the radiationless relaxation. The intensity ratio of fluorescence from the *m*-th (I_m) and that of *n*-th (I_n) ($m<n$) is given by

$$\frac{I_n}{I_m} = \frac{k_{im}}{k_{em}} \Phi_{en} \prod_{j=m+1}^{n} \left(1 - \Phi_{ej}\right) \frac{F_n}{F_m} \qquad (1)$$

Here k_{im} and k_{em} are the phonon-emission rate and radiative rate from the *m*-th vibronic level. Φ_{ej} is the fluorescence quantum efficiency from *j*-th level. Φ_{en} is the efficiency from the *n*-th level and F_n and F_m are the Franck-Condon factors. By assuming common $k_{ij} \equiv k_i$ and $k_{ej} \equiv k_e$ for all $j=m, \ldots, n$ levels. The equation (1) can be simplified as follows.

$$\frac{I_n}{I_m} \cong \left(1 - \Phi_e\right)^{m-n} \frac{F_n}{F_m} \qquad (2)$$

Here Φ_e is the common quantum yield of phonon emission ($=k_e/(k_e+k_i)$). The above assumption of the common k_{ij} can be justified because of the large values of *j*, even though the rate is proportional to (*j* + 1). The value of *n*-*m* is estimated to be 7.4 using the *m*-th and *n*-th excitation energy being 2.18 and 1.89 eV and phonon frequency of 316 cm^{-1}. Then τ_0 is estimated as 122 fs, which is nearly twice of oscillation period of 316 cm^{-1} (M-X stretching mode). The ratio of Franck-Condon factors can be obtained from $\tau_{\mathrm{eff}\,n}/\tau_{\mathrm{eff}\,m}$ and I_n/I_m, the result being shown in Table 1. If we can obtain the Franck Condon factors from $j = 0$ to some large value, they can be used to analyze the potential curve along the geometrical relaxation. We are now in a process of studying the dependence of the lifetime on the probe wavelength.

Table 1. Lifetimes, relative intensities and relative Franck-Condon factors at four differnt vibrational quantum numbers

j	hν/eV	$\tau_{\mathrm{eff}\,j}$/fs	I_j/I_{jo}	F_j/F_{jo}
26.3 ($\equiv j_o$)	2.18	270	1.5	$\equiv$ 1.0
23.5	2.07	580	1.6	2.0
20.9	1.97	780	1.8	2.4
18.9	1.89	1200	2.0	3.3

In conclusion, we have observed fluorescence from the nonrelaxed MX CT-excitons and determined the decay time of the nonequibrium excitons for the first time. The emission life from the CT exciton during the geometrical relaxation which causes anomalously large Stokes shift was measured for the first time.

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