

Time-resolved luminescence study of self-trapped-exciton relaxation in quasi-one-dimensional halogen-bridged mixed-valence metal complexes

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The relaxation processes of self-trapped excitons (STE's) in halogen-bridged mixed-valence metal complexes (*MX*-chain complexes) have been investigated by picosecond time-resolved luminescence measurements. The self-trapped exciton luminescence of $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ (*en* = ethylenediamine) decays exponentially with a lifetime of 230 ± 10 psec at 2 K. The STE's are dominantly annihilated nonradiatively by tunneling and thermally activated processes. In an *MX* complex with ligand disorder caused by the random arrangement of the *R,R* and *S,S*-isomer ligand molecules, the STE's exhibit nonexponential decay. The decay dynamics varies with energy across the luminescence band and depends on the photon energy of the excitation laser. This behavior is explained by site-selective generation of STE's and their subsequent hopping relaxation.

I. INTRODUCTION

The halogen-bridged mixed-valence metal complexes (*MX*-chain complexes) are considered to be a prototype material for studies of the optical properties of one-dimensional electronic systems.¹ In *MX*-chain complexes metal ($M = \text{Pt}, \text{Pd}, \text{and Ni}$) and halogen ($X = \text{Cl}, \text{Br}, \text{and I}$) ions form one-dimensional chains as depicted in Fig. 1.² The metal ions are surrounded by ligand molecules such as ethylenediamine (*en*) and cyclohexanediamine (*chxn*). In Pt and Pd complexes, the halogen distortions from the central position of the neighboring metal ions cause charge-density waves (CDW's) with periods of twice the metal-metal distance.^{3,4} Since the CDW ground state in the *MX*-chain complexes has twofold degeneracy as in polyacetylene,^{5,6} the investigation of the relaxation processes of the photoexcited states in these materials has gained considerable interest from a funda-

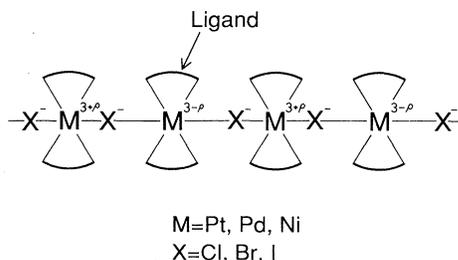


FIG. 1. Chain structure of *MX*-chain complexes ($0 \leq \rho \leq 1$).

mental point of view.^{1,7-28} One interesting feature of the *MX*-chain complexes is that the physical properties, such as the energies of the CDW band gaps and the magnitudes of the halogen ion distortions, can be changed in a wide range by substitution of the metal, the halogen, the counter ions, and the ligand molecules.^{1,9,28-30} Additionally, single crystals can be easily prepared.

The electronic excitation across the CDW band gap, which corresponds to a charge-transfer excitation from the $M^{3-\rho}$ metal ion to the neighboring $M^{3+\rho}$ metal ions, can be observed as an intense charge-transfer (CT) excitation absorption band polarized parallel to the chain axis.^{9,31-35} If photoexcited states are generated in these complexes, they are considered to relax immediately into lattice relaxed states like self-trapped excitons (STE's), solitons, and polarons, due to the large lattice instability of these systems in the excited state.^{1(c),24,36,37} Since there is no potential barrier between free excitons and STE's in a one-dimensional system,^{36,37} the relaxation into the self-trapped state is expected to occur on a very short time scale.

When an *MX*-chain complex is excited within the absorption band, a broad luminescence band at about half the CT-exciton energy arises.⁷⁻⁹ This luminescence band has been attributed to the radiative recombination of STE's. The observed large Stokes shift is thought to be a characteristic feature of the CDW system.^{1(c)} However, only a few experiments on the relaxation dynamics of STE's in *MX*-chain complexes have been reported so far.^{13,14}

We have investigated the dynamics of the relaxation

processes of STE's in *MX*-chain complexes by picosecond time-resolved luminescence measurements. In particular, the dependence of the luminescence decay on excitation energy, detection energy, and temperature was studied.

Extensive research has been devoted to the photoexcited states in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4 [\text{Pt}(\text{en})\text{-Cl}]$, which is one of the well-known *MX*-chain complexes.^{8,9,11,12,14,15,18,33-35} We have measured the time-resolved luminescence of this complex as a prototype material. Our experimental results show that the luminescence decay in Pt(en)-Cl is exponential with a time constant of about 230 psec. The decay is controlled by a temperature-independent tunneling process and a thermally activated process.

Recently, extensive studies have been made on the effects of disorder in the relaxation processes of excitons in one-dimensional π - and σ -conjugated polymers with small polaronic effects.³⁸⁻⁴² On the other hand, little is known about the effects of disorder in the exciton relaxation in one-dimensional systems with large polaronic effects such as *MX*-chain complexes. In order to investigate the role of disorder in *MX*-chain complexes, we have compared two different model systems: $[\text{Pt}(\text{rac-chxn})_2][\text{Pt}(\text{rac-chxn})_2\text{Cl}_2](\text{ClO}_4)_4 [\text{Pt}(\text{rac-chxn})\text{-Cl}]$ and $[\text{Pt}(1R,2R\text{-chxn})_2][\text{Pt}(1R,2R\text{-chxn})_2\text{Cl}_2](\text{ClO}_4)_4 [\text{Pt}(R,R\text{-chxn})\text{-Cl}_2]$. The chair form chxn has two optical isomers: 1*R*,2*R*-chxn and 1*S*,2*S*-chxn. In Pt (rac-chxn)-Cl the ligands consist of a 1:1 mixture of 1*R*,2*R*-chxn and 1*S*,2*S*-chxn molecules, which are randomly arranged. This causes disorder in the one-dimensional chains. On the other hand, the ligand molecules in Pt-(*R*,*R*-chxn)-Cl are all of the type 1*R*,2*R*-chxn. Thus such disorder is absent. By comparison of the results for Pt-(*R*,*R*-chxn)-Cl and Pt-(rac-chxn)-Cl, we demonstrate that disorder in the one-dimensional chains affects considerably the dynamics of STE's in *MX*-chain complexes.

II. EXPERIMENT

Single crystals of *MX*-chain complexes were obtained from water solution with 1-2 wt % HClO_4 by slow evaporation. The time-integrated luminescence spectra of single crystals of *MX*-chain complexes have been measured using a cw Ar-ion laser and a high-pressure Hg lamp, respectively, as excitation light sources. In the time-resolved luminescence measurements the samples were either excited by laser pulses of a cw mode-locked Ar-ion laser or by a synchronously pumped dye laser. In the case of Ar-ion laser excitation the photon energies were 2.41 and 2.60 eV, respectively, with a pulse duration of about 150 psec. The duration of the dye-laser pulses was about 5 psec. Dye-laser light pulses were used in the case of an excitation photon energy 2.31 eV. Photon energies ranging from 2.8 to 3.4 eV were obtained via frequency doubling of the dye-laser pulses. The luminescence was passed through a monochromator and then detected by a streak camera with a time resolution of 20 psec.

III. RESULTS AND DISCUSSION

A. Pt-(en)-Cl

The component polarized parallel to the chain axis of the imaginary part of the dielectric constant (ϵ_2) of Pt(en)-Cl and the luminescence spectra polarized parallel and perpendicular to the chain axis are shown in Fig. 2. The ϵ_2 spectrum was obtained from reflection spectra by Kramers-Kronig transformation. The component of ϵ_2 perpendicular to the chain axis is considerably smaller and lies within the error caused by the slight roughness of the as-grown surface (0.2) in the energy range shown here. The intense absorption band at 2.72 eV polarized parallel to the chain axis in the ϵ_2 spectrum is attributed to the CT-exciton transition. The luminescence band at 1.22 eV has been attributed to the radiative recombination of STE's.^{8,9} In contrast to the CT-exciton absorption band, the luminescence polarized perpendicular to the chain axis has considerable intensity and can be clearly resolved.

In Pt-(en)-Cl the intensity of the luminescence polarized perpendicular to the chain axis is about 25% of that parallel to the chain axis. The shape and the spectral position of the luminescence bands of the STE's are the same in both components. Additionally, no polarization dependence of the luminescence lifetime was found. Thus we have to conclude that the luminescence arises from the same STE state in both cases. This leads to the conclusion that the transition dipole moment of the STE is inclined to the chain axis (more than 26°). Such a polarization behavior is commonly observed in the STE luminescence of *MX*-chain complexes. This is quite different from the CT-exciton absorption bands and the photoinduced absorption bands which are attributed to solitons or polarons.^{10,11} These absorption bands are strongly polarized parallel to the chain axis. In order to rotate the transition dipole moment, lattice distortion of the *MX* chain in the direction perpendicular to the chain axis must occur in the STE state. If we assume that the wave function of the STE's is extended over many metal sites, the perpendicular component of the STE luminescence is expected to be very small. Therefore, we conclude that the wave function of the STE is confined to a

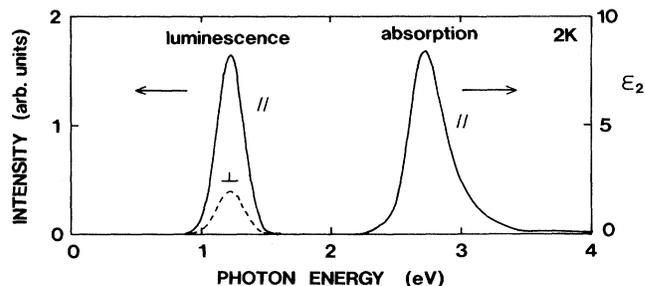


FIG. 2. Imaginary part of the dielectric constant (ϵ_2) and the luminescence spectra for an excitation photon energy of 2.54 eV of Pt(en)-Cl at 2 K for polarization parallel (solid line) and perpendicular (broken line) to the chain axis.

small number of metal sites. This is consistent with theoretical studies, which predicts that STE's are extended over only five metal sites.^{1(c),26} The excitation photon energy dependence of the STE luminescence has been measured for excitation photon energies ranging from 2.41 to 3.40 eV. No energy shift of the luminescence band has been observed.

The luminescence decay in Pt-(en)-Cl is shown in Fig. 3 for two different emission photon energies. The lower curve in Fig. 3 depicts the time behavior of the luminescence at an emission energy of 1.36 eV. A time constant of 230 ± 10 psec can be deduced from the exponential decay. This decay time is almost constant for different detection energies within the luminescence band. Only at the very-high-energy side of the spectrum does an additional fast component limited by the time resolution appear for a detection energy of 1.52 eV, as can be seen in the upper part of Fig. 3. This fast component has been attributed to the radiative decay of the CT excitons during the relaxation to the STE states.^{7,13,14} Figure 4 summarizes the results for the luminescence-decay constants as a function of emission photon energy. (The initial fast decay of the luminescence at the highest energies is not considered here.) As can be clearly seen, the decay constant is independent of the detection energy within the experimental error ($\pm 5\%$). The luminescence decay of Pt-(en)-Cl for excitation energies of 2.31, 2.41, and 2.60 eV has been measured. No obvious excitation-energy-dependent change of the lifetime is detected.

The temperature dependence of the luminescence decay times is shown in Fig. 5. The lifetimes are constant at low temperature but decrease with increasing temperature above 40 K. This observation suggests that the STE's are annihilated by a superposition of a temperature-independent process and a thermally ac-

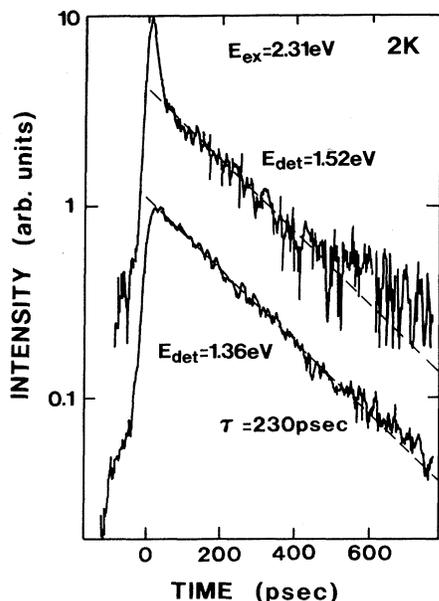


FIG. 3. Luminescence decay of Pt-(en)-Cl at 2 K detected at 1.52 and 1.36 eV.

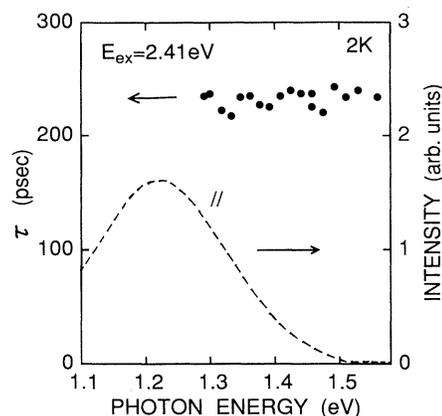


FIG. 4. Relation between detection energy and lifetime of the STE luminescence of Pt-(en)-Cl at 2 K for an excitation photon energy of 2.41 eV. The dashed line is the time-integrated luminescence spectrum.

tivated process. The temperature dependence of the lifetime τ can then be expressed as

$$\tau = [\tau_0^{-1} + A \exp(-\varepsilon/KT)]^{-1}. \quad (1)$$

Here, τ_0^{-1} is a temperature-independent decay rate, ε is the activation energy, and A is a constant corresponding to the rate at high temperatures. The solid line in Fig. 5 shows the best fit based on (1). Good agreement with the experimental data is found if an activation energy of 15 meV is assumed.

The luminescence lifetime of Pt-(en)-Cl at low temperature is 230 psec. If we assume that the lifetime of the STE is determined by the radiative lifetime, the oscillator strength of the STE can be estimated as follows:

$$\tau_r = \frac{3c^3 m \hbar^2}{2e^2 E_{em}^2 n f}. \quad (2)$$

Here, τ_r is the radiative lifetime, n is the refractive index, f is the oscillator strength of the STE, E_{em} is the peak energy of STE luminescence band, and c is the velocity of

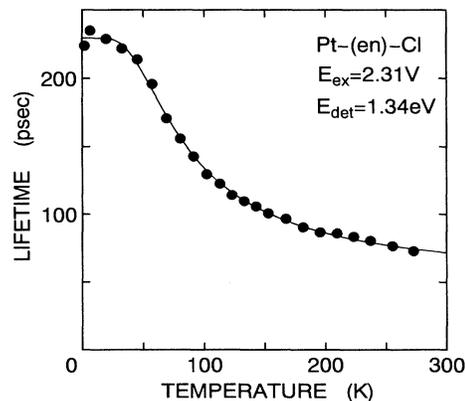


FIG. 5. Temperature dependence of the lifetime of the STE luminescence of Pt-(en)-Cl detected at 1.34 eV for an excitation photon energy of 2.31 eV.

light. Substituting the values $\tau_r = 230$ psec, $E_{em} = 1.22$ eV, and $n = 2$, as obtained in our experiments, we can calculate the oscillator strength of the STE in Pt-(en)-Cl to be 1.0×10^2 . This is more than 30 times larger than that of the CT exciton ($f = 3.0$ defined for a $M^{3+\rho}-X-M^{3-\rho}-X$ unit)⁹ and it seems to be too large for a STE.

We rule out a much higher oscillator strength of the STE's, since a significant enhancement requires delocalization of the exciton wave function. This is in contradiction with our experimental findings in Fig. 2 and theoretical studies.^{1(c),26} Therefore, we conclude that the annihilation of the STE's is dominated by a nonradiative process. This is in agreement with the recently reported value of 0.025 for the quantum efficiency of the STE luminescence in Pt-(en)-Cl.¹⁴ Since the lifetimes of the STE's in Pt-(en)-Cl do not show a sample dependence, the nonradiative annihilation processes are probably of intrinsic origin.

We mention that an even faster decay of STE's has been observed in π -conjugated polymers like polydiacetylene and polythiophene.⁴³ The temperature dependence of the lifetime indicates that the nonradiative annihilation of the STE's is thermally activated with a barrier height of about 15 meV. In theoretical work Mishima and Nasu have pointed out the importance of soliton-pair formation in MX -chain complexes.²⁴ We consider the formation of soliton pairs from STE's to be one of the dominant nonradiative decay channels.

We also mention that our experimental findings are different from those of Tanino, Rühle, and Takahashi,¹⁴ who have reported lifetimes around 100 psec, dependent on the detection energy. We could not measure the luminescence decay for the excitation photon energy used in their experiment ($E_{ex} = 2.13$ eV), since in our experiment the luminescence intensities were too small. However, since this energy is below the absorption edge of the CT exciton (about 2.3 eV at low temperature),^{11,33} it might be possible that absorption by defect states plays a significant role at this photon energy. In our experiment, all excitation photon energies were located within the CT-exciton absorption band.

B. Pt-(rac-chxn)-Cl and Pt-(R,R-chxn)-Cl

We now turn to the comparison of the recombination dynamics in MX -chain complexes with and without ligand disorder in the one-dimensional chains. Reflection spectra at room-temperature and low-temperature luminescence spectra of the disordered Pt-(rac-chxn)-Cl and ordered Pt-(R,R-chxn)-Cl for polarization parallel to the chain axis are shown in Fig. 6. The peak structures in the reflection spectra of Pt-(rac-chxn)-Cl (dotted line) and Pt-(R,R-chxn)-Cl (solid line) at 3.2 and 3.1 eV are assigned to CT-exciton transitions. The peak energies of the CT-exciton absorption bands are located close to the peak energy of the reflection bands in MX complexes.^{9,34} This is due to the broad linewidths of the CT-exciton absorption bands. The slight difference in the CT-exciton energies of these two complexes is consistent with the difference in the bond distances shown in Table I.⁴⁴ The halogen distortion of Pt-(rac-chxn)-Cl is slightly larger

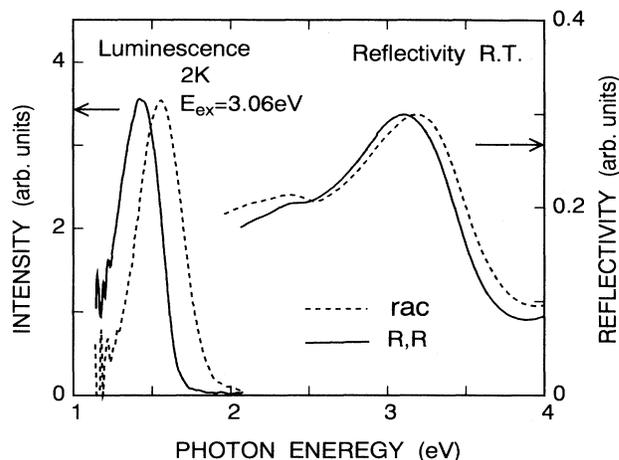


FIG. 6. Room-temperature polarized reflection spectra and luminescence spectra at 2 K for an excitation photon energy of 3.06 eV of Pt-(R,R-chxn)-Cl (solid line) and Pt-(rac-chxn)-Cl (broken line) for polarization parallel to the chain axis.

than that of Pt-(R,R-chxn)-Cl. The luminescence bands seen in Fig. 6 are caused by radiative recombination of STE's.

The excitation photon energy dependence of the peak energies of the STE luminescence bands are shown in Fig. 7. In the case of low-energy excitation ($E_{ex} < 2.71$ eV) the energy shifts of the luminescence bands of both complexes are attributed to the site-selective generation of strongly localized CT-exciton states located in the lower-energy tails of the absorption bands. In Pt-(R,R-chxn)-Cl, the peak energy of the STE luminescence band is independent of the excitation photon energy in the energy range from 2.85 to 3.40 eV. This energy range corresponds to the intense CT-exciton absorption band. Pt-(rac-chxn)-Cl behaves differently. The emission energy shifts with the excitation energy over the entire range. Such behavior is different from that observed in conjugated polymers such as poly(*p*-phenylenevinylene)'s^{38,40} and polysilylenes.³⁹ In these polymer films the exciton luminescence bands do not show an energy shift for the excitation photon energy above a certain demarcation energy.

The time evolution of the STE luminescence of Pt-(R,R-chxn)-Cl for an excitation photon energy of 2.96 eV has been measured. A decay time of about 70 ± 5 psec is deduced in the detection-energy range from 1.48 to 1.80 eV. No detection-energy dependence of the lifetime was observed in the energy range. Similar to Pt-(en)-Cl, a very fast decay component limited by the time resolution occurs for detection at the very-high-energy side.

TABLE I. Bond distances (\AA). R = Pt^{IV}-Cl/Pt^{II}-Cl.

	Pt ^{II} -Pt ^{IV}	Pt ^{II} -Cl	Pt ^{IV} -Cl	R
Pt-(R,R-chxn)-Cl	5.719(1)	3.401(4)	2.318(4)	0.682
Pt-(rac-chxn)-Cl	5.730(1)	3.418(7)	2.312(7)	0.676

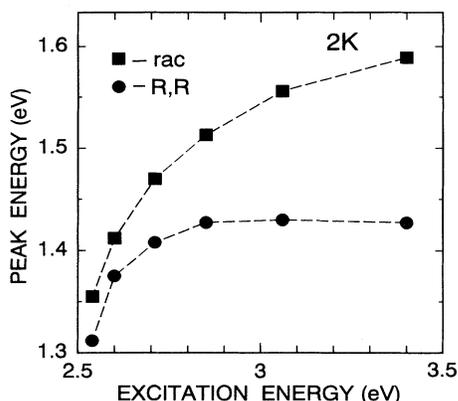


FIG. 7. Excitation photon energy dependence of the peak energies of the self-trapped exciton luminescence in Pt-(rac-chxn)-Cl and Pt-(*R,R*-chxn)-Cl complexes.

The time evolution of the STE luminescence of Pt-(rac-chxn)-Cl for an excitation photon energy of 2.96 eV is shown in Fig. 8. In contrast to the results in Pt-(*R,R*-chxn)-Cl, the STE luminescence of the Pt-(rac-chxn)-Cl shows a nonexponential decay. In addition, the decay depends significantly on the detection energy. The relation between the detection photon energy and the time t_1 required for the STE luminescence of the Pt-(rac-chxn)-Cl to decay from 80% to 80/e% of the maximum value is shown in Fig. 9 for three different excitation photon energies. It can be seen that t_1 decreases as the detection energy increases in the cases of $E_{\text{ex}}=2.96$ and 3.20 eV. In the case of $E_{\text{ex}}=2.80$ eV, the detection-energy dependence of t_1 is quite small. It is also obvious from the data shown in the figure that t_1 increases for decreasing E_{ex} .

For the interpretation of these experimental results the role of disorder in *MX*-chain complexes has to be considered. Substitution of the ligand molecule causes large changes of the CDW gap in *MX*-chain complexes due to the change of the steric conformation or the change of the hydrogen bond network.^{28,30} Such effects are seen ex-

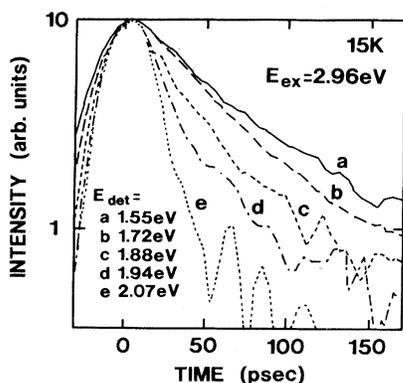


FIG. 8. Luminescence decay of Pt-(rac-chxn)-Cl at 15 K detected at different emission photon energies for an excitation photon energy of 2.96 eV.

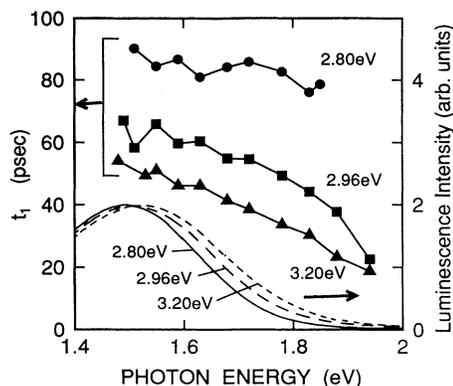


FIG. 9. Detection-energy dependence of t_1 and the luminescence spectra of the Pt-(rac-chxn) complex at 15 K for excitation photon energies of 2.80, 2.96, and 3.20 eV.

perimentally in the energy difference of 0.4 eV between the CT-exciton peak energy of Pt-(en)-Cl (Fig. 2) and that of Pt-(*R,R*-chxn)-Cl (Fig. 7). The random alignment of the two isomer molecules in Pt-(rac-chxn)-Cl causes a large inhomogeneous energy distribution of both the CT-exciton states and the STE states. Similarly, relaxation dynamics of excitons within an inhomogeneously broadened exciton density of states (DOS) has been investigated in inorganic semiconductors⁴⁵ and π - (Refs. 38 and 41) and σ - (Ref. 39) conjugated polymers.

The specific differences in the relaxation behavior of Pt-(en)-Cl, Pt-(*R,R*-chxn)-Cl and Pt-(rac-chxn)-Cl can be explained by the different amount of disorder present in the different samples. If we assume a close correlation between the excitation energy and the position of the STE within the inhomogeneously broadened DOS, we can interpret the results in terms of hopping relaxation of STE's.

STE's are formed immediately after photoexcitation into the center of the absorption band ($E_{\text{ex}}=3.20$ eV). Since there is no evidence that the rise time is longer than the time resolution of our system, we conclude that the STE-formation time is less than 20 psec. We therefore attribute the dynamics monitored in our time-resolved luminescence measurement to the subsequent hopping relaxation of the STE's within their DOS. This predicts a faster decay rate at the high-energy side of the luminescence band. If the excitation energy is lowered, the energy relaxation rate decreases due to the reduced number of final states to which the STE can hop. When a STE is generated in the lower-energy tail of the DOS ($E_{\text{ex}}=2.80$ eV), the STE can hardly hop at all during its lifetime. Consequently, no detection photon energy dependence of the decay rate is expected. Due to the hopping motion, the nonradiative annihilation of the STE may be enhanced. This enhancement may be caused by defects or by the realignment of the lattice distortion during the hopping motion.

Hence the nonradiative annihilation probability is high for the STE's generated close to the center of the DOS as compared to those STE's which are generated in the

lower-energy tail of the DOS. The STE's are annihilated before downward hopping is completed due to the slowing energy relaxation and efficient nonradiative annihilation. As a result, the STE luminescence spectrum depends on the excitation energy. Since the hopping motion of the STE's must be accompanied by a lattice distortion, it is reasonable that the hopping rate of STE's in *MX*-chain complexes is much smaller than in conjugated polymers like polysilylenes³⁹ and poly(*p*-phenylvinylene)'s,⁴² where only small polaronic effects occur.

IV. SUMMARY

We have investigated the dynamical relaxation processes of the STE's in *MX*-chain complexes by picosecond time-resolved luminescence measurements. In *MX*-chain complexes with ordered chains, the STE luminescence exhibit single exponential decays. The lifetimes of the STE's are 230 and 70 psec at low temperature in Pt-(en)-Cl and Pt-(*R,R*-chxn)-Cl, respectively. Such short lifetimes are due to efficient nonradiative annihilation of

STE's. The STE's are annihilated by a temperature-independent tunneling process and by a thermally activated process with a small potential barrier of about 15 meV determined in the case of Pt-(en)-Cl. These results are consistent with recent theoretical calculations of the potential surfaces of the ground and the excited states of *MX*-chain complexes.^{24,26} In the disordered *MX* chain, the energy positions of the STE luminescence bands and the lifetimes of the STE's show a pronounced excitation photon energy dependence. The lifetimes of the STE's also depend on the detection energy. Such a behavior of the STE luminescence can be described qualitatively by the site-selective generation of STE's and the subsequent interplay of hopping relaxation and nonradiative annihilation processes.

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