Pressure Dependence of Phosphorescence through Energy Transfer from Inorganic Quantum Well to Naphthalene Chromophore in \((C_{10}H_{7}C_{2}H_{4}NH_{3})_{2}PbCl_{4}\)

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Abstract. The organic-inorganic hybrid quantum well compound, \((C_{10}H_{7}C_{2}H_{4}NH_{3})_{2}PbCl_{4}\), exhibits enhanced phosphorescence due to the energy transfer from the excitonic state of inorganic quantum well to the triplet state of naphthalene chromophore. In the present study, photoluminescence and optical absorption spectra of \((C_{10}H_{7}C_{2}H_{4}NH_{3})_{2}PbCl_{4}\) were investigated under pressure to 6.5 GPa in order to investigate the pressure dependence of the energy transfer. The phosphorescence intensity decreases with pressure up to 5 GPa, while the energy of the triplet state of naphthalene chromophore does not change with pressure. From the absorption spectra under pressure, it is found that the exciton energy of inorganic quantum well decreases with pressure up to 5 GPa. In our experiment, the energy transfer from the singlet state of naphthalene chromophore exited by ultraviolet light at 3.82 eV to the singlet exciton of inorganic quantum well occurs, and then the singlet exciton is converted to the triplet exciton by intersystem crossing, which is followed by the energy transfer to the triplet state of naphthalene chromophore for phosphorescence. Our observations on phosphorescence can be explained by a change in the energy difference between the excitonic state of inorganic quantum well and the singlet state of naphthalene chromophore with pressure.

1. Introduction
Lead halide-based organic-inorganic hybrid compounds having the general formula, \((RNH_{3})_{2}PbX_{4}\), are composed of a two dimensional semiconducting sublattice of corner-sharing \([PbX_{6}]^{4-}\) octahedra separated by insulating organic layers of \(RNH_{3}^{+}\) (X: Cl, Br and I, R: alkylchain or \(\pi\)-conjugated chromophore). The inorganic sublattice plays a role as multi-quantum wells for carriers and excitons, since the lead halide layers have a narrower band gap than the HOMO-LUMO gap of the organic layers. These lead halide-based quantum well compounds exhibit a stable exciton with a large exciton binding energy [1].

Lead halide-based compounds with a naphthalene chromophore have been reported to exhibit enhanced phosphorescence from the naphthalene chromophore [2, 3], and have drawn attention due to a potential use as light emitting devices. Both the reports have dealt with phosphorescence caused by energy transfer from the excitonic state in the inorganic quantum well to the triplet state of the naphthalene chromophore. In addition, lead chloride-based organic-inorganic hybrid quantum well compounds with a naphthalene chromophore have an excitonic state of inorganic quantum well whose energy is close to that of the singlet state of naphthalene chromophore.
The exciton energy of the lead iodide-based organic-inorganic hybrid quantum well compound, \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbI}_4\), was reported to decrease with pressure [4]. Likewise, in lead chloride-based quantum well compounds the exciton energy of inorganic quantum well and the energy of naphthalene chromophore can be changed with pressure, so that the phosphorescence through the energy transfer between them can be tuned. In the present study, we have investigated the pressure dependences of photoluminescence (PL) and optical absorption spectra of a lead chloride-based organic-inorganic hybrid quantum well compound with a naphthalene chromophore, \((\text{C}_{10}\text{H}_7\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4\), and with an alkylammonium molecule, \((\text{C}_3\text{H}_7\text{NH})_2\text{PbCl}_4\), in comparison, and discussed the pressure dependence of energy transfer.

2. Experimental

Single crystals of \((\text{C}_{10}\text{H}_7\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4\) and \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbCl}_4\) were grown by a solution method. In \((\text{C}_{10}\text{H}_7\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4\), 2-(1-naphthyl)ethylamine hydrochloride and \text{PbCl}_2 were mixed in dimethylformamide (DMF) and kept at room temperature for a couple of weeks. We confirmed that the samples exhibited a quantum well structure by X-ray diffraction. The samples were loaded into a hole (300 µm in diameter) in a stainless steel gasket and pressurized quasi-hydrostatically using a diamond anvil cell with Fluorinert (FC-40) as a pressure medium up to 6.5 GPa. A ruby chip was used as a pressure calibrator. PL and absorption spectra were measured under pressure at room temperature. The 325 nm line of a He-Cd laser was used for PL measurements as the excitation light source.

3. Results and Discussion

Changes in the PL spectra of \((\text{C}_{10}\text{H}_7\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4\) and \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbCl}_4\) with pressure are shown in Fig. 1(a) and 1(b), respectively. We observed the excitonic emission from lead chloride quantum well at 3.7 eV in the PL spectrum of \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbCl}_4\) at ambient pressure (not shown in Fig. 1(b)). The excitonic emission decreases in energy with pressure to 3.4 eV at 3.7 GPa, as shown in Fig. 1(b). The spectrum exhibits a defect-induced broad emission around 2.5 eV. On the other hand, the PL spectrum of \((\text{C}_{10}\text{H}_7\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4\) does not exhibit the excitonic emission but the phosphorescence from the naphthalene chromophore, as noted by A, B, C and D in Fig. 1(a). In our experiment, the fluorescence from the naphthalene chromophore was also observed, as shown by the bands E and F in Fig. 1(a), due to our strong excitation regime, whereas it was not observed in the previous report [3]. The observations indicate that the phosphorescence of \((\text{C}_{10}\text{H}_7\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4\) is induced by the energy transfer from the excitonic state of inorganic quantum well to the triplet state of naphthalene chromophore.

![Figure 1](image-url)
While the phosphorescence intensity of \( (C_{10}H_2C_7N_2H_2)^4PbCl_4 \) decreases with pressure, the fluorescence intensity increases with pressure. The peak energies of the emission bands do not change very much up to 5 GPa, indicating that the energies of triplet and singlet states of naphthalene chromophore are not affected significantly by applying pressure.

In Fig. 2, a change in the absorption spectrum of \( (C_{10}H_2C_7N_2H_2)^4PbCl_4 \) with pressure is shown. A steep rise in the optical density originates from the edge of an absorption band due to exciton in the lead chloride layer. In Fig. 3, the exciton energy is plotted as a function of pressure by solid squares. The exciton energy decreases linearly with pressure up to 5 GPa (the pressure coefficient: -50 meV/GPa) and then increases with further applying pressure. We also obtained the pressure coefficient of the exciton band in \( (C_8H_{17}N_2H_2)^3PbCl_4 \) to be -58 meV/GPa. The red-shifts can be explained mainly by the elevation of the valence band maximum with pressure due to its antibonding nature between Pb-6s and Cl-3p orbitals [5]. The phosphorescence intensity in \( (C_{10}H_2C_7N_2H_2)^4PbCl_4 \) is also shown in Fig. 3 by solid circles. Similarly, the phosphorescence intensity decreases linearly with pressure up to 5 GPa, and then becomes constant. The results suggest that the pressure dependence of the phosphorescence intensity of naphthalene chromophore is associated with the change in the exciton energy of inorganic quantum well under pressure.

The energy transfer of lead halide-based organic-inorganic hybrid quantum well compounds with naphthalene chromophore was discussed at ambient pressure [3, 6]. In the model in Ref. [3], the singlet state of naphthalene chromophore is excited optically. The excited energy of naphthalene chromophore transfers to the lead halide quantum well to create a Wannier-like singlet exciton. Then, the singlet exciton is converted to a triplet exciton by intersystem crossing [7]. The energy of the triplet exciton in lead halide quantum well transfers to the triplet state of naphthalene chromophore efficiently [6] for phosphorescence.

Let us discuss our data on the pressure dependence of phosphorescence from naphthalene chromophore in the light of the above model of energy transfer. In our experiment, the singlet state of naphthalene chromophore, \( (S_1)_{\text{napht}} \), and the singlet excitonic state of the lead chloride quantum well,
(S$_1$)$_{\text{inorg}}$, are excited simultaneously by ultraviolet light at 3.82 eV at ambient pressure, as shown in Fig. 4. Since the energy of (S$_1$)$_{\text{naph}}$ does not change with pressure whereas the energy of (S$_1$)$_{\text{inorg}}$ decreases with pressure, the energy difference between them increases with pressure. As a result, the energy transfer from (S$_1$)$_{\text{naph}}$ to (S$_1$)$_{\text{inorg}}$ is suppressed under pressure, while the fluorescence from (S$_1$)$_{\text{naph}}$ is enhanced. Consequently, after the intersystem crossing ((S$_1$)$_{\text{inorg}}$ $\rightarrow$ (T$_1$)$_{\text{inorg}}$) in the lead chloride quantum well, the energy transfer from the triplet exciton of the lead chloride quantum well, (T$_1$)$_{\text{inorg}}$, to the triplet state of naphthalene chromophore, (T$_1$)$_{\text{naph}}$, is suppressed so that the phosphorescence intensity decreases with pressure.

There is another channel for energy transfer which leads to phosphorescence from naphthalene chromophore under pressure; (S$_1$)$_{\text{inorg}}$ $\rightarrow$ (T$_1$)$_{\text{inorg}}$ $\rightarrow$ (T$_1$)$_{\text{naph}}$ after the optical excitation of the lead chloride quantum well which follows relaxation to (S$_1$)$_{\text{norg}}$. In our photoluminescence excitation (PLE) measurements on (C$_{10}$H$_7$C$_2$H$_4$NH$_3$)$_2$PbCl$_4$ at ambient pressure, the intensity of the excitonic emission, seen as a sharp peak in Fig. 1(b), does not change very much with excitation energy from 3.82 eV to 4.08 eV (the application of pressure to 5 GPa on (C$_{10}$H$_7$C$_2$H$_4$NH$_3$)$_2$PbCl$_4$ places the position of excitation energy to the conduction band almost equivalent to 4.08 eV at ambient pressure). The result indicates that the contribution from this channel to our high pressure phosphorescence data on (C$_{10}$H$_7$C$_2$H$_4$NH$_3$)$_2$PbCl$_4$ would not change very much with pressure. Thus, our observation on the pressure dependence of phosphorescence, i.e. the depression of the phosphorescence intensity, comes mainly from the decoupling between (S1)$_{\text{naph}}$ and (S1)$_{\text{inorg}}$ by pressure.

**Figure 4.** Change in the energy diagram with pressure for (C$_{10}$H$_7$C$_2$H$_4$NH$_3$)$_2$PbCl$_4$. The broken lines indicate the level excited by ultraviolet light at 3.82 eV in the present experiment.

4. **Conclusion**

We measured PL and optical absorption spectra of (C$_{10}$H$_7$C$_2$H$_4$NH$_3$)$_2$PbCl$_4$ and (C$_8$H$_{17}$NH$_3$)$_2$PbCl$_4$ under pressure at room temperature. The energy relation between the excited states of organic and inorganic parts changes with pressure. As a result, the intensities of both fluorescence and phosphorescence of (C$_{10}$H$_7$C$_2$H$_4$NH$_3$)$_2$PbCl$_4$ are changed with pressure. Our observations on PL spectra under pressure can be explained by a decrease in the energy transfer due to an increase in the energy difference between the excitonic state of inorganic quantum well and the singlet state of naphthalene chromophore with pressure. The present study opens up a possibility to control phosphorescence by pressure-tuning of energy transfer between organic and inorganic parts.

5. **References**
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