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Charge-transfer transitions between wires and spacers in an inorganic-organic quasi-one-dimensional crystal methylviologen lead iodide

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We have studied the optical property and electronic structure of an inorganic-organic quasi-one-dimensional crystal, methylviologen lead iodide. Two absorption bands were observed in the near ultraviolet and visible regions. The one is an absorption band at 3.1 eV with a large oscillator strength, which is assigned to one-dimensional excitons confined in the inorganic chains. The other is a broad band observed between 2.0 and 2.8 eV and attributed to charge-transfer transitions from the lead iodide chains to the methylviologen molecules. From the luminescence excitation spectra, it is found that there are two kinds of charge-transfer transitions from the valence band and the nonbonding state of the inorganic chains to the lowest unoccupied molecular orbital of methylviologen.

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Charge-transfer transitions between wires and spacers in one-dimensional semiconductors and insulators lead to the formation of spatially separated electron-hole pairs. In consequence, the wires are doped with a single type of charge carriers (electrons or holes). The carrier doping by such charge-transfer transitions is intriguing for optical control of band filling of nonconducting chains and resultant electric properties. However, there are only a few reports on the charge-transfer transitions between wires and spacers, using semiconductor heterostructures.[1,2] In this work, our attention has been paid to inorganic-organic quasi-one-dimensional materials for investigations of the charge-transfer transitions.

Inorganic-organic quasi-one-dimensional lead-iodide compounds consist of inorganic chains and intervening organic molecules.[3] The electronic properties of inorganic chains that are comprised of face-sharing lead-iodide octahedra have been studied using piperidinium lead-iodide, $(C_5H_{10}NH_2)PbI_3$.[4–7] It is reported that one-dimensional excitons in the inorganic wires are very stable even at room temperature with a large binding energy of 0.36 eV.[6] Recently, another quasi-one-dimensional lead-iodide crystal with the methylviologen (MV) molecules, which is well-known as a strong electron acceptor,[9] has been synthesized and the crystal structure has been investigated by Tang *et al.*[8] The crystal has a structure, in which the inorganic chains of face-sharing lead iodide octahedra are surrounded with the methylviologen molecules, as shown in Fig. 1(a).

In this paper, we report on charge-transfer transitions between the inorganic chains and the organic spacer molecules (methylviologen) in the inorganic-organic quasi-one-dimensional crystal, methylviologen lead iodide $(MV)Pb_2I_6$. The followings have been found by the experiment. (1) The charge-transfer transitions from the lead iodide chains to methylviologen exist in the energy region lower than the intrachain transitions. (2) Two kinds of charge-transfer transitions take place from the valence band and the nonbonding state of the inorganic chains to the lowest unoccupied molecular orbital of methylviologen.

The material was synthesized by mixing of the dimethyl sulfoxide solutions of methylviologen iodide (MVI_2) and lead iodide (PbI_2) at the equimolar ratio at room temperature. Dark red single crystals with a shape of a hexagonal column and typical dimensions of $0.3 \times 0.3 \times 1\ \mathrm{mm}^3$ were obtained by slow evaporation of the solvent. The crystal color is much different from that (pale yellow) of piperidinium lead iodide, whose optical properties in the visible and near ultraviolet regions are governed by intrachain electronic transitions. The result indicates that optical reflection and absorption appear in the visible region by the usage of methylviologen as a spacer molecule. By x-ray diffraction measurement, the crystal structure was confirmed to be the same as the reported one,[8] as shown in Fig. 1(a). Optical reflectance measurement was carried out with a single crystal and absorption measurement with a single crystal cleaved using adhesive tapes at room temperature. Photoluminescence and photoluminescence excitation spectra were measured with single crystals cooled at 4 K in a helium cryostat, which were excited with Xe-lamp light monochromated by a subtractive double monochromator. In all the experiments, a charge-coupled device (CCD) camera cooled by liquid nitrogen and equipped with a polychromator was used as a light detector, and the incident light was shed on the sample with $k \perp c$.

Optical absorption and photoluminescence spectra are shown in Fig. 2. The inset shows polarized reflectance spectra with the incident light polarizations of $E//c$ and $E \perp c$. In

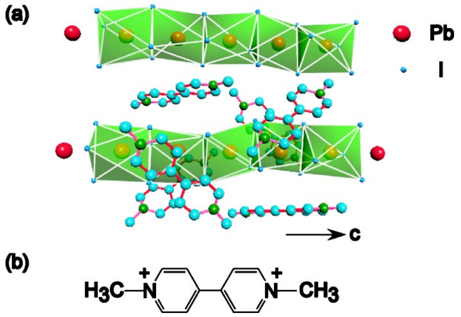

FIG. 1. (Color online) The crystal structure (a) of $(MV)Pb_2I_6$ that was obtained by our x-ray crystal structure analysis and the molecular structure (b) of methylviologen (MV). All of the hydrogen atoms of methylviologen are omitted in (a) for clarity. The average Pb-I distance is ~3.3 Å.

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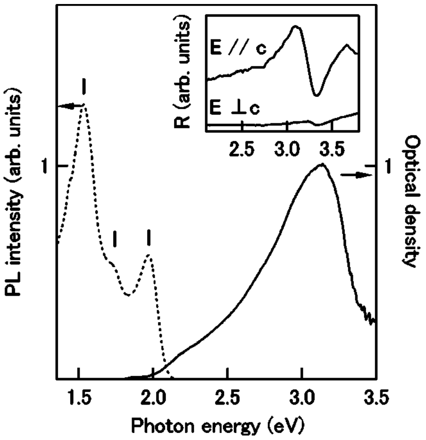

FIG. 2. Optical absorption (solid line) and photoluminescence spectra (broken line) of the (MV)Pb_2I_6 crystal. For the luminescence spectrum, the excitation photon energy is 2.88 eV. The inset shows polarized reflectance spectra for the incident light polarizations of $E//c$ and $E \perp c$ (see text).

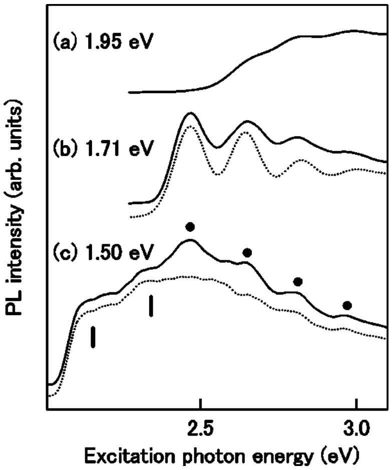

FIG. 3. Photoluminescence excitation spectra (solid lines) of the (MV)Pb_2I_6 crystal. The left numbers denote the detected luminescence energies (see text).

the absorption spectrum, two kinds of optical absorption bands are observed. The one is a strong absorption band peaked at 3.1 eV and the other is a broad one with a small oscillator strength in the energy range of 2.0–2.8 eV. In the polarized reflectance spectra in the inset, a strong reflection peak that corresponds to the absorption band at 3.1 eV is observed at 3.11 eV for the incident light polarization parallel to the chain direction (c axis). The energies of the strong absorption and reflection peaks and the polarization dependence of the optical reflection are almost in agreement with those of the lowest-energy one-dimensional excitons in the lead iodide chains that consist of face-sharing lead iodide octahedra.[4–6] From the result, the optical absorption at 3.1 eV is assigned to the lowest excitons in the inorganic chains. On the other hand, the latter broad absorption in the visible region cannot be ascribed to the internal transitions of the lead iodide chains and methylviologen, since the one-dimensional exciton is the lowest excitation[10] of the chains and intramolecular electronic transitions of methylviologen are in the near ultraviolet region ($\geqslant$4.0 eV).[11,12] The absorption band is considered to be due to charge-transfer transitions from the negatively charged inorganic chains to the positively charged methylviologen molecules.

In the photoluminescence spectrum, three emission bands of two peaks at 2.0 and 1.5 eV and one shoulder at 1.7 eV are observed, as displayed with the vertical bars in Fig. 2. It is reported that one-dimensional excitons in the lead iodide chains relax to self-trapped excitons rapidly and a luminescence band peaked at around 2.0 eV with a spectral width of ~0.3 eV is observed.[5,6] Thus, the emission band peaked at 2.0 eV is assigned to a self-trapped exciton in the inorganic chains.

In order to examine the two photoluminescence bands observed at 1.5 and 1.7 eV, the excitation spectra of the three emission bands were measured and are shown in Fig. 3. The excitation spectrum of the emission at 1.95 eV exhibits luminescence increase in the energy region higher than 2.6 eV. Although the exciton absorption occurs at around 3.1 eV, the luminescence is also observed with the excitation energy between 2.6 and 3.0 eV. The optical transition below around 3.0 eV will be discussed later. On the other hand, at a glance, the excitation spectra of the emissions at 1.71 and 1.50 eV are different from that of the self-trapped exciton luminescence in the point that those photoluminescence's increase with optical absorptions in the visible region, which correspond to the charge-transfer transitions from the wires to methylviologen. In the excitation spectrum (b), the absorption edge is at 2.4 eV and there is a distinct vibrational structure. The Stokes shift is estimated as ~0.7 eV. The excitation spectrum (c) has an absorption edge at 2.05 eV and shows a relatively broad spectrum. The energy of the absorption edge is in agreement with that of the absorption spectrum in Fig. 2. The Stokes shift is obtained to be ~0.6 eV.From these results, it is indicated that there exist two kinds of charge-transfer transitions from the inorganic chains to methylviologen. From the large Stokes shifts, the lower-lying emissions at 1.5 and 1.7 eV are attributed to the polaron pairs generated by lattice relaxations of the spatially separated electron-hole pairs created by the two charge-transfer transitions.

Here, we describe the band structures of the lead iodide chains and methylviologen to discuss the excitation spectra (b) and (c). The electronic structures of the lead iodide chains and methylviologen are illustrated in Fig. 4, where V.B. and C.B. denote the valence and conduction bands, respectively, and N.B. stands for the nonbonding state and Ex for the one-dimensional exciton. The valence band of the lead-iodide chains consists of the 6s orbitals of the Pb^{+2} ions and the 5p orbitals of the I^- ions, and the conduction band is mainly comprised of the 6p orbitals of the Pb^{+2} ions. The nonbonding state consists of the 5p orbitals of the I^- ions, which direct perpendicularly to the c axis. From the band calculation and photo-electron spectroscopic study of the lead iodide wires, it is reported that an occupied nonbonding state locates by ~0.5 eV below the top of the valence band, as shown in Fig. 4, and that the band width is much smaller than that (~0.4 eV) of the valence band.[7] As for the organic moiety, the valence and conduction bands are comprised of

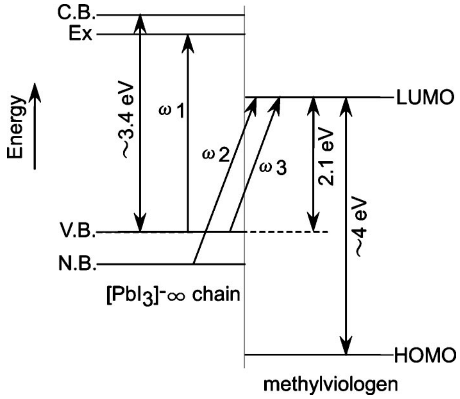

FIG. 4. Energy diagram of the electronic structure of the (MV)Pb_2I_6 crystal. For the inorganic chains, the horizontal lines labeled with C.B. and V.B. denote the bottom of the conduction band and the top of the valence band, respectively. N.B. stands for the nonbonding state and Ex for the one-dimensional exciton (see text).

the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), respectively. Since the HOMO and LUMO are π and π^* molecular orbitals, respectively, which expand perpendicularly to the molecular planes, the transfer integrals between the neighboring molecules are very small and, therefore, the band widths of the conduction and valence bands are considered to be very small as compared to that of the valence band of the inorganic chains. From those facts, it is seen that two charge-transfer transitions occur from the nonbonding state and the valence band of the wires to LUMO of methylviologen. In Fig. 4, those transitions are designated by ω_2 and ω_3, respectively, and that of the one-dimensional exciton by ω_1.

On the basis of the above discussion, it is envisaged that the excitation spectra (b) and (c) are attributed to the charge-transfer transitions from the nonbonding state and the valence band of the inorganic chains to LUMO of methylviologen, respectively. Since the nonbonding state of the wires and LUMO of methylviologen have very small band widths, the excitation spectrum (b) was analyzed within a framework of a local excitation model, using the following equation, [13] $I(E)=A_0e^{-S}\Sigma_n(S^n/n!)g_0(E-E_0-n\hbar\omega,\Gamma_0)+A_1g_1(E-E_1,\Gamma_1)$, in which $g(E,E_0,\Gamma)$ is a Gaussian function peaked at E_0 with a full-width at half-maximum of Γ, and S is the Huang-Rhys factor denoting the strength of the electron-lattice coupling. The first term of the equation designates the optical absorption spectrum due to the transitions from the vibrational ground state of the nonbonding state to the vibrational ground and vibrationally excited states of LUMO. Here, a single vibrational mode in LUMO of methylviologen with an angular frequency of ω is supposed. The second term expresses the absorption spectrum of the one-dimensional exciton in the wires. The contribution results from nonradiative relaxation processes from the one-dimensional exciton to the initial state for the luminescence at 1.71 eV. The calculated spectrum is shown by the dotted curve in Fig. 3(b), and the parameters were obtained as follows, $S=0.82$, $\hbar\omega=0.175$ eV, $E_0=2.466$ eV, $E_1=3.1$ eV, $A_0/A_1=4.5$, $\Gamma_0=0.118$ eV, and $\Gamma_1=0.745$ eV. It is seen that the calculated curve reproduces well the experimental one. The energy of the vibrational mode is by far larger than that of LO phonons in the lead iodide chains, which is estimated as around a few meV. In the Raman spectra of a one-electron reduced methylviologen monocation, a molecular vibrational mode with ~190 meV that is close to the obtained value (175 meV) is strongly observed.[14–16] Thus, the vibrational structure is attributed to the molecular vibrational mode of methylviologen. Conversely, the appearance of the vibrational structure of one-electron reduced methylviologen in the excitation spectrum evidently reveals that the photocreated electrons are located at the methylviologen molecules and occurrence of the charge-transfer transition.

On the other hand, although the excitation spectrum (c) includes contributions of optical absorptions shown by the excitation spectra (a) and (b), the luminescence increase at the energy lower than 2.4 eV is considered to be due to the charge-transfer transition from the valence band of the inorganic chains to LUMO of the methylviologen molecules. The vibrational structure marked by solid circles in Fig. 3(c) is attributed to the charge-transfer transition from the nonbonding state of the wires to LUMO of methylviologen. We have tentatively subtracted it using the first term of $I(E)$ with the parameters obtained above. The resultant spectrum is shown by the dotted curve in Fig. 3(c). The large spectral width is considered to originate from the valence band width (~0.4 eV)[7] of the wires and the molecular vibrations of methylviologen. Two steps marked by the vertical bars are observed with an interval of ~190 meV, which is close to the vibrational energy (175 meV) estimated from the excitation spectrum (b), and attributed to the molecular vibration of methylviologen. The results obtained from the photoluminescence excitation spectra (b) and (c) are summarized as follows. (1) In the both spectra, the vibrational structures by the molecular vibrational mode in LUMO of methylviologen are observed. (2) Energy difference (0.4 eV) in onsets between the two spectra is almost in agreement with the reported energy gap (~0.5 eV)[7] between the top of the valence band and the nonbonding state. (3) The spectrum (b) is reappeared well within a framework of a local excitation model, and the spectrum (c) has a larger spectral width than the spectrum (b). From these results, it is concluded that the excitation spectra (b) and (c) are attributed to the charge-transfer transitions from the nonbonding state and the valence band of the chains to LUMO of methylviologen, respectively.

The remaining question is the assignment of the optical absorption between 2.6 and 3.0 eV observed in the excitation spectrum (a). We interpret it in terms of nonradiative relaxations from vibrationally excited states of spatially separated electron-hole pairs to self-trapped excitons in the wires. In the energy region, a weak vibrational structure is observed with the same peak energies as that in the spectrum (b), although the peak-intensity distribution is much different. The observation of the vibrational structure indicates the contribution of the ω_2 transition via the nonradiative relaxation.

In conclusion, we have found that the charge-transfer transitions from the inorganic chains to the methylviologen molecules occur in the lower energy region than the one-dimensional exciton in the inorganic-organic pseudo-one-dimensional crystal, methylviologen lead iodide. From the analysis of the luminescence excitation spectra, it is shown that there exist two kinds of charge-transfer transitions from the valence band and the nonbonding state of the inorganic chains to LUMO of methylviologen.

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