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# Photoconductivity induced by wire-to-spacer charge-transfer transitions in an inorganic-organic hybrid quasi-one-dimensional crystal: Polaron excitation in the Urbach tail

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Photocurrent excitation spectra have been measured as a function of applied electric field and temperature with crystals of an inorganic-organic hybrid quasi-one-dimensional compound, methylviologen lead iodide, which consists of lead iodide chains and methylviologen spacer molecules. Photocurrent is induced dominantly by charge-transfer transitions from the lead iodide chains to methylviologen in the energy region between 2.1 and ~2.7 eV. Furthermore, the photoconductivity parallel to the inorganic chains is enhanced remarkably in the low-energy absorption tail of the charge-transfer transition, but not for the perpendicular current direction. It is revealed that the photocurrent enhancement is associated with the excitation in the Urbach tail of the charge transfer transition, which gives rise to electrons localized on methylviologen and hole polarons in the lead iodide chains. The photoconductivity enhancement is discussed and explained by the one-dimensional transport of photocreated hole polarons.

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## I. INTRODUCTION

Charge carriers in one-dimensional systems have gained considerable interest, because of unique electronic and transport properties due to the low dimensionality.[1–3] In one dimension, charge carriers created just after photoexcitation relax to polarons immediately via an electron-lattice coupling.[4] It has been reported that one-dimensional polarons behave like a soliton, so-called solitonlike polarons, which have very high mobility of the order of $10^5$ cm$^2$/V sec even at room temperature.[5–10]

Recently, it has been reported that photoconductivity in one-dimensional organic polymers is enhanced significantly by photoinduced charge separation between polymers and spacers with large electron affinity such as a fullerene molecule ($C_{60}$) (Refs. 14–18) and inorganic nanosized dots (CdS and CdSe) (Refs. 19,20). The charge separation takes place via nonradiative relaxations from intracomponent excited states. In consequence, electrons and holes are created outside and inside polymers, respectively. The spatial separation of geminate carriers, which leads to long carrier lifetimes and weakening of electron-hole scattering, is considered to be a cause of the high photoconductivity.

In this work, we have studied photoconductivity induced by charge-transfer transitions between wires and spacers in crystals of an inorganic-organic hybrid quasi-one-dimensional compound, methylviologen lead iodide. As shown in Fig. 1(a), all the negatively charged inorganic chains of face-sharing lead iodide octahedra $[\mathrm{PbI}_3]_\infty^-$ are aligned parallel to the $c$ axis and the positively charged organic molecules, methylviologen (MV), are embedded among the inorganic chains, as spacer molecules.[21] Methylviologen has large electron affinity with a charge of 2+ and is well known as an electron acceptor.[22] The molecular structure is shown in the lower part of Fig. 1(a). Recently, we have found that charge-transfer transitions from the lead iodide chains to methylviologen take place in the visible region, being the lowest-energy transition.[23] Via the charge-transfer transition, the inorganic chains are doped transiently with a single type of charge carriers (holes) and electrons are trapped on methylviologen. The wire-to-spacer charge-transfer transition is considered to be interesting not only for realizing high photoconductivity, but also for studies of photocarriers in one-dimensional systems. We have measured photocurrent excitation spectra as a function of applied electric field and temperature, and observed that photocurrent is predominantly induced by the wire-to-spacer charge-transfer transition. Furthermore, the photoconductivity along the inorganic chains is enhanced in the low-energy absorption tail. We discuss the photoconductivity enhancement in terms of the one-dimensional transport of hole polarons.

## II. EXPERIMENT

The compound was synthesized by a chemical solution method according to the literature.[23] Dark red, single crystals with a shape of a hexagonal column and typical dimensions of $0.2\times0.2\times0.5$ mm$^3$ were obtained by slow evaporation of the solvent, dimethyl sulfoxide (DMSO). The crystal structure was analyzed by x-ray diffraction measurements and found to be the same as that reported in Ref. 21. The crystallographic $c$ axis, which is parallel to the lead iodide chains, was confirmed to coincide with the direction of the longest dimension of the crystal, as shown in Fig. 1(b). The samples used in the measurement of photoconductivity parallel ($I//c$) and perpendicular ($I\perp c$) to the lead iodide chains are illustrated schematically in Fig. 1(b). As shown in the figure, two gold wires with a diameter of 15 $\mu$m were attached on the irradiated crystal surface, using carbon paste, with a gap of 60 (electrode width)$\times$200 (distance between electrodes) $\mu$m$^2$ for $I//c$ and $200\times150$ $\mu$m$^2$ for $I\perp c$. The resistance without light irradiation in those samples was estimated to be more than 100 M$\Omega$ for both the current directions, which indicates that the material is an insulator.

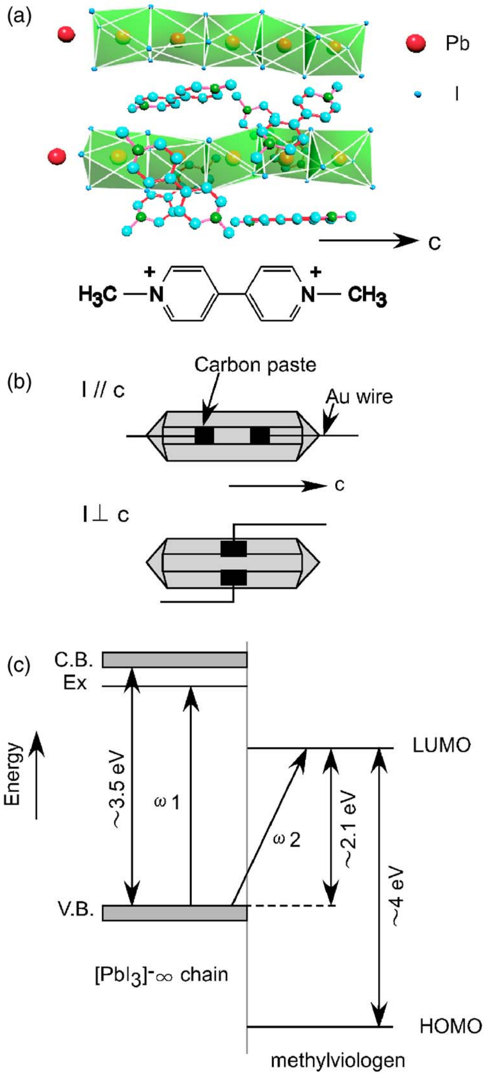

FIG. 1. (Color online) (a) Perspective view of the crystal structure of methylviologen lead iodide, (b) schematic picture of the samples in the photoconductivity measurements for $I//c$ and $I\perp c$, and (c) schematic energy diagram of the electronic structure of methylviologen lead iodide. In (a), the molecular structure of methylviologen is shown below the crystal structure. In (c), C.B. and V.B. denote the conduction and valence bands, respectively. "Ex" stands for one-dimensional excitons. LUMO and HOMO, respectively, designate the lowest unoccupied and highest occupied molecular orbitals. The arrows labeled with $\omega_1$ and $\omega_2$ stand for excitonic and charge-transfer transitions, respectively. See text.

Steady-state photocurrent was measured by detecting the voltage across a $10\ \mathrm{M}\Omega$ load resistor connected in series to the sample using a digital multimeter with application of dc voltage. Nonpolarized monochromated Xe-lamp light was applied almost normally on the area between the electrodes entirely. The light power was less than $2\ \mathrm{mW/cm^2}$ at any photon energy. Photocurrents measured with different excitation photon energies were corrected to photocurrent per excitation photon number, using a Xe-lamp light spectrum measured by calibrated photodiode.[24] Optical absorption spectra were measured with a halogen lamp and a charge-coupled device (CCD) camera cooled by liquid nitrogen and equipped with a polychromator. In all the experiments, the sample was set in a temperature-controlled cryostat with a helium compressor.

## III. ELECTRONIC STRUCTURE

The schematic energy diagram of the electronic structure of methylviologen lead iodide is shown in Fig. 1(c). For the lead iodide chains, the band gap is reported to be 3.5 eV and the bandwidths of the conduction and valence bands to be ∼0.4 eV (Refs. 25–28). An intrachain excitonic transition lies at 3.1 eV, as shown by the arrow marked with $\omega_1$. The exciton binding energy is as large as 0.36 eV and, thus, excitons exist even at room temperature.[26,27] For methylviologen, the bandwidths of the lowest unoccupied (LUMO) and highest occupied molecular orbitals (HOMO) are considered to be negligibly small, as compared to those (∼0.4 eV) of the conduction and valence bands of the lead iodide chains. The molecular transitions are reported to be above the near-ultraviolet region ($\geqslant$4.0 eV) (Refs. 29,30). In addition to those intracomponent transitions, there exist charge-transfer transitions from the lead iodide chains to methylviologen in the visible region, as shown by the arrow marked with $\omega_2$. The onset of the charge-transfer transition is reported to be approximately at 2.1 eV (Ref. 23).

## IV. RESULTS

Optical absorption spectrum of the cleaved thin crystal and excitation spectra of photocurrent parallel ($I//c$) and perpendicular ($I\perp c$) to the chain direction ($c$ axis) with static electric field of ∼250 V/cm and ∼330 V/cm, respectively, were measured at room temperature, as shown in Fig. 2. Just above the absorption spectrum, a vertically magnified spectrum around 2.2 eV is displayed. In the absorption spectrum, a prominent peak at 3.1 eV and a broad continuous band between 2.0 and ∼2.7 eV are observed. As reported in Ref. 23, the assignment is carried out as follows. The strong absorption peak at 3.1 eV is attributed to excitons confined in the lead iodide chains, and the weak broadband in the visible region between 2.0 and ∼2.7 eV to the charge-transfer transition from the lead iodide chains to methylviologen. The absorption bandwidth of the wire-to-spacer charge-transfer transition is due to the bandwidth (∼0.4 eV) of the valence band of the lead iodide chains and excitation of electrons to higher-energy molecular vibrational levels of LUMO of methylviologen. As displayed by the arrow, a shoulder edge of the charge-transfer transition is located at ∼2.17 eV. The energy (2.17 eV) is close to the onset (∼2.1 eV) of the charge-transfer transition. Below 2.17 eV, there is a long tail due to phonon scatterings of the charge-transfer transition, which will be described later. It is noted that the absorption tail is not attributed to the exciton absorption in the inorganic chains, which disappears almost at ∼2.7 eV. For the thick sample used for photocurrent measurements mentioned below, optical density is higher than unity above 2.0 eV, as will be shown in Fig. 5.

In the photocurrent excitation spectra shown in Fig. 2(b), the ordinate value is photocurrent per incident photon num-

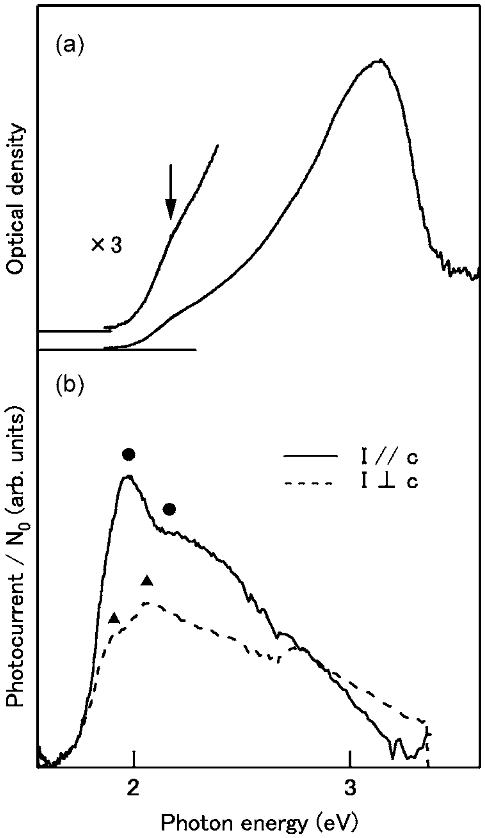

FIG. 2. (a) Optical absorption spectrum of the cleaved crystal and (b) excitation spectra of photocurrent per incident photon number ($N_0$) with applied electric field of ~ 250 V/cm for $I//c$ (solid line) and ~ 330 V/cm for $I \perp c$ (broken line) at room temperature. The arrow indicates the energy position at 2.17 eV, the solid circles those at 1.97 and 2.16 eV, and the triangles those at 1.91 and 2.06 eV.

ber ($N_0$). For $I//c$, the photocurrent rises up around 1.8 eV, has a prominent peak at 1.97 eV and a shoulder at 2.16 eV, as displayed by the circles in the figure, and decreases with increasing excitation photon energy.[32] For $I \perp c$, a low-energy shoulder at 1.91 eV and a peak at 2.06 eV are observed, as displayed by the triangles. Since the crystals used were very tiny, for the sample in the measurement of $I \perp c$, the electrodes were attached not only on the top crystal face, but also on other tilted faces, as shown in Fig. 1(b). For this reason, it is difficult to compare those spectra so quantitatively. Nevertheless, we saw experimentally that the photocurrent is larger for $I//c$ than that for $I \perp c$, as shown in Fig. 2(b). By comparison to the absorption spectrum, the photocurrent band in the energy region between 2.16 and ~2.7 eV for $I//c$ and the whole band up to ~2.7 eV for $I \perp c$ are ascribed to the wire-to-spacer charge-transfer transition. Above ~2.7 eV, both the intrachain excitonic transition and the higher-energy charge-transfer transition probably contribute to the photoconductivity. It is indicated that photocurrent for $I//c$ and $I \perp c$ is predominantly induced by the wire-to-spacer charge-transfer transition. Moreover, it is seen that photoconductivity is enhanced in the absorption tail of the charge-transfer transition for $I//c$, but not for $I \perp c$. The enhancement of photoconductivity is not due to the slightly different applied electric fields for those spectra. Hereafter, we concentrate on the photoconductivity along the inorganic chains.

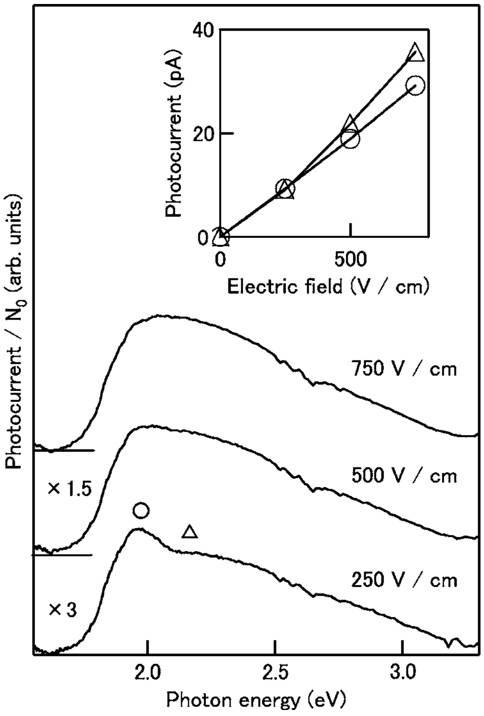

FIG. 3. Excitation spectra of photocurrent along the inorganic chains per excitation photon number ($N_0$) at room temperature with various applied electric fields displayed on the right-hand side. The open circle and triangle indicate the energy positions at 1.97 and 2.16 eV, respectively. The inset shows the electric-field dependence of the photocurrent at 1.97 and 2.16 eV by open circles and triangles, respectively.

The excitation spectra of photocurrent along the inorganic chains measured with various electric fields at room temperature are shown in Fig. 3. The electric-field dependence of the photocurrent at 1.97 and 2.16 eV is plotted in the inset. From the spectra, it is seen that with increasing electric field the photocurrent above 2.16 eV increases more than that at 1.97 eV, and that the peak structure at 1.97 eV is indiscernible at 750 V/cm. The result indicates that the bands at 1.97 eV and above 2.16 eV exhibit different electric-field dependences. As shown in the plots, the photocurrent at 1.97 eV is linear to the applied electric field. On the other hand, the one at 2.16 eV increases superlinearly with electric field. From the linear and superlinear dependences, the quantum efficiency of mobile photocarriers to incident photon number is considered to be much less than unity in the electric-field region,[31] which suggests that the electron-hole binding energy is much larger than the thermal energy ($k_B T$=25 meV at 295 K).

Figure 4 shows the excitation spectra of photocurrent along the inorganic chains measured at various temperatures with applied electric field of ~750 V/cm. It is seen that the photocurrent is decreased drastically with decreasing temperature. As for the spectral dependence, the photocurrent around 1.97 eV is reduced with lowering temperature much more than that above 2.16 eV, revealing the different temperature dependences for the two bands. As shown by the

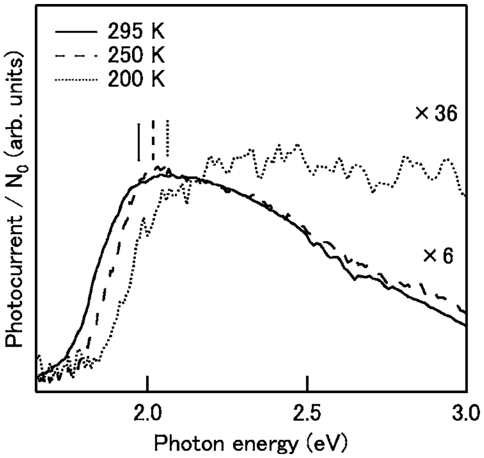

FIG. 4. Excitation spectra of photocurrent along the inorganic chains with electric field of 750 V/cm at 295 (solid line), 250 (broken line), and 200 K (dotted line). The solid, broken, and dotted vertical lines show the energy positions at 1.97, 2.01, and 2.06 eV, respectively. The ordinate value in the spectra at 250 and 200 K is magnified 6 and 36 times, respectively.

vertical bars, the edges shift to the high-energy side with decrease of temperature; 1.97 eV at ~295 K, 2.01 eV at 250 K, and 2.06 eV at 200 K. The drastic decrease of the photocurrent above 2.16 eV suggests that mobile carriers are generated via thermal ionization of photocreated electron-hole pairs with an activation energy larger than the thermal energy ($k_BT$=25 meV at 295 K), which agrees with the result obtained from the electric-field dependence.

Optical absorption spectra around 2.0 eV were measured at various temperatures, as shown in Fig. 5 (Ref. 33). The optical density in the absorption tail of the wire-to-spacer charge-transfer transition decays almost exponentially as the photon energy decreases. It is seen that the slope is increased with decreasing temperature. From the result, the exponentially decaying absorption tail is interpreted in terms of the Urbach rule that originates from electron-phonon interactions, rather than that due to impurities or defects. The absorption tails are analyzed by using the equation of the Urbach rule,[2] $I(E)=I_0\exp[\sigma\beta(E-E_0)]$, in which $\sigma$ is a steepness constant, $E_0$ is a converging energy, and $\beta=(k_BT)^{-1}$ at sufficiently high temperature. The parameters obtained from the fitting to the data are plotted as a function of inverse temperature in the inset of Fig. 5. The converging energy ($E_0$) remains almost constant (2.15 - 2.16 eV) against temperature. The value is in good agreement with the energy gap (~2.1eV) of the wire-to-spacer charge-transfer transition. The value of $\sigma\beta$ is increased with the inverse of temperature sublinearly. The steepness constant is tentatively estimated from the data at room temperature to be ~0.35, assuming that $\beta=(k_BT)^{-1}$. Note that the value is slightly underestimated, since even at room temperature the assumption is not held exactly. However, the value is remarkably small as compared to those (0.6 - 3) reported for other inorganic semiconductors and insulators,[2] which indicates that an electron-lattice coupling in the quasi-one-dimensional compound is quite strong. It has been demonstrated that the electron-lattice coupling in analogous lead iodide chains is very strong.[26,27] Therefore, the electron-lattice coupling is considered to be due to photocreated holes in the inorganic chains. The temperature dependence of the absorption tails is compared to that of the photoconductivity excitation spectra. In the absorption spectra, the photon energy, at which the optical density is 0.79, is 1.97 eV at 295 K, 1.99 eV at 250 K, and 2.02 eV at 200 K. The high-energy shift well corresponds to that observed in the photoconductivity excitation spectra displayed by the three bars in Fig. 4. The decrease of photocarrier density resulted from the reduction of absorption coefficient in the absorption tail with temperature is a cause of the drastic change of the photocurrent around 1.97 eV. From the experiment, it is indicated that the photoconductivity enhancement around 1.97 eV is associated with the excitation in the Urbach tail of the wire-to-spacer charge-transfer transition.

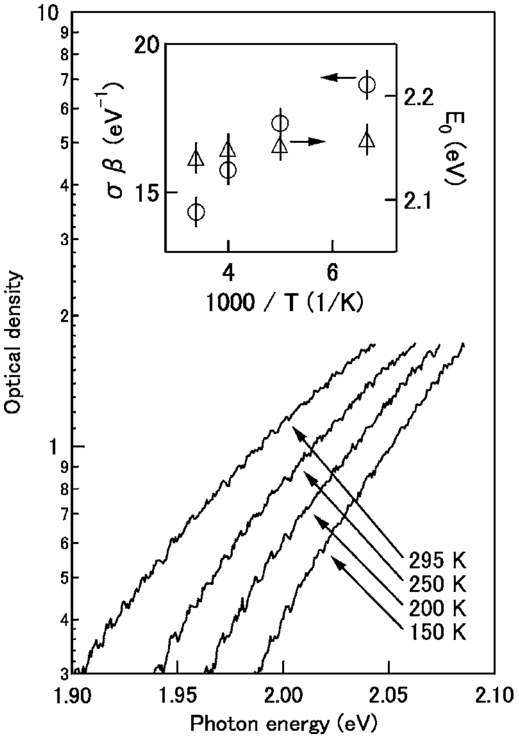

FIG. 5. Optical absorption spectra around 2.0 eV at various temperatures displayed on the right-hand side. The inset shows the temperature dependences of $\sigma\beta$ (open circles) and $E_0$ (open triangles) (see text).

## V. DISCUSSION

We discuss the photoconductivity enhancement in the Urbach tail of the wire-to-spacer charge-transfer transition. It is well known that the Urbach tail is ascribed to excited states in phonon fields, or momentarily lattice-trapped excited states.[2,34] Taking into account that the absorption tail is mainly due to interactions of holes with phonons, the optical transition in the Urbach tail creates a pair of electrons on methylviologen and hole polarons in the lead iodide chains. The electrons are localized on methylviologen, since the bandwidth of LUMO is considered to be smaller than the thermal energy. The photocurrent enhancement is interpreted in terms of the one-dimensional transport of hole polarons in the inorganic chains, assuming hopping between the chains to be much slower than the propagation along the chains. The assumption is considered to be reasonable, since the lead iodide chains are separated with methylviologen.

The similar phenomena that photoconductivity increases in absorption tails have been observed in a number of inorganic and organic materials even without adding impurities.[31,35,36] Most of them have been explained in terms of short lifetime of photocarriers near the crystal surface due to defects.[31,35,36] At present we consider that the shoulder at 1.91 eV for $I \perp c$ and low-energy shift of the peak at 2.06 eV for $I \perp c$, as compared to the shoulder at 2.16 eV for $I // c$, are possibly due to the surface effect. However, the photoconductivity enhancement with large one-dimensional anisotropy cannot be explained by the effect.

It is reported in one-dimensional organic polymers, which have no charge-transfer transitions between wires and spacers, that photocurrent is strikingly enhanced in the absorption tail of intrachain transitions, which is well below the energy of band gaps or excitons.[11–13] Although the phenomena have been discussed with lattice-relaxed carriers such as polarons and solitons, they have not been clarified yet. Our result suggests a possibility that the phenomena can be understood in the same scenario as follows. Photoexcitation in the absorption tail of intrachain electronic transitions generates, directly and efficiently, a pair of lattice-relaxed electrons and holes, whereby photoconductivity that is predominantly due to polaron transport increases in the absorption tail. We consider that the phenomenon observed here is characteristic of one-dimensional systems with a strong electron-lattice coupling, in which polarons play an important role in charge transport.

For the photoconductivity with the excitation photon energy higher than 2.16 eV, the one-dimensional anisotropy is less than that in the absorption tail, as shown in Fig. 2. Taking into account the one-dimensional transport of hole polarons, the photocurrent for $I // c$ and $I \perp c$ is considered to be due to different photocarriers; for $I // c$ hole polarons in the lead iodide chains, and for $I \perp c$ electrons on methylviologen. Further investigations are in progress.

## VI. CONCLUSION

Photoconductivity excitation spectra in an inorganic-organic hybrid quasi-one-dimensional compound, methylviologen lead iodide have been measured as a function of electric field and temperature. Photoconductivity is induced predominantly by charge-transfer transitions from the lead iodide chains to methylviologen. It is observed that the photoconductivity is remarkably enhanced in the Urbach tail of the wire-to-spacer charge-transfer transition for $I // c$, but not for $I \perp c$. The photoconductivity enhancement is explained by the one-dimensional transport of hole polarons in the inorganic chains.

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