| Title     | Optical characterization of platinum-halide ladder compounds |
|-----------|-------------------------------------------------------------|
| Author(s) | Yamamoto, Shoji; Ohara, Jun                                |
| Citation  | Physical Review B, 76(23), 235116                         |
| Issue Date| 2007                                                        |
| Doc URL   | http://hdl.handle.net/2115/32339                          |
| Rights    | ©2007 The American Physical Society                        |
| Type      | article                                                    |
| File Information | PhysRevB_76_235116.pdf                                      |

Hokkaido University Collection of Scholarly and Academic Papers: HUSCAP
Optical characterization of platinum-halide ladder compounds

Shoji Yamamoto and Jun Ohara

Department of Physics, Hokkaido University, Sapporo 060-0810, Japan

(Received 18 June 2007; revised manuscript received 24 July 2007; published 14 December 2007)

Varieties of quasi-one-dimensional halogen (X)-bridged transition-metal (M) complexes, \( (\text{C}_2\text{H}_4\text{N}_2) \times [\text{Pt}(\text{en})\text{Br}]_2 (\text{en}=\text{ethylenediamine}) \) and (bpy) \( \times [\text{Pt}(\text{en})\text{Br}]_2 (\text{en}=\text{ethylendiamine}) \) and (bpy), exhibiting photo- and pressure-induced phase transitions, 18–22 whereas its analogs have recently succeeded in assembling single-chain compounds, while the former variety, whose interchain valence arrangement is out of phase, is reminiscent of conventional MX single-chain compounds, the while, versus variety, whose interchain valence arrangement is in phase, reveals itself as a d-p-\( \pi \)-hybridized multiband ladder material.

I. INTRODUCTION

Quasi-one-dimensional transition-metal (M) complexes with bridging halogens have been attracting much interest for several decades, and significant efforts are still devoted in fabricating their new varieties. Conventional platinum-halide chains exhibit a Peierls-distorted mixed-valent ground state, while their nickel analogs have a Mott-insulating monovalent regular-chain structure. Palladium-halide ladders are intermediates with a ground state tunable optically and electrochemically. The charge-density wave (CDW) ground state can be tuned by halogen doping and pressure application as well. Metal binucleation leads to a wider variety of electronic states. A diplatinum iodide chain compound, \([\text{C}_2\text{H}_4\text{H}_2\text{NH}_2]_2 [\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_2]_4\), exhibits photo- and pressure-induced phase transitions, whereas its analog without any counter ion, \( \text{Pt}_2(\text{CH}_3\text{CS}_2)_2 \), is of metallic conduction at room temperature and undergoes successive phase transitions with decreasing temperature. There are further attempts to bridge polynuclear and/or heterometallic units by halogens.

More than 300 MX compounds have thus been synthesized so far, but their crystal structures are all based on MX single chains. In such circumstances, several authors have recently succeeded in assembling MX compounds within a ladder lattice. Metal oxide ladders are generally remarkable for their strongly correlated d electrons. \( \text{SrCu}_2\text{O}_3 \), behaves as a d-p ladder of the Hubbard type, whereas \( \text{NaV}_2\text{O}_5 \) is well describable within a single-band Holstein-Hubbard Hamiltonian. On the other hand, the newly synthesized metal-halide ladders are double featured with competing electron-electron and electron-phonon interactions and are possibly of d-p-\( \pi \)-mixed character. Such a multicolored stage potentially exhibits a variety of electronic states, and it is highly interesting to control them chemically and physically. Thus motivated, we make a model study of ladder-shaped MX compounds, \( (\mu\text{-bpy}) \times [\text{Pt}(\text{en})\text{Br}]_2 \times [\text{ClO}_4] \times \text{H}_2\text{O} (\text{X}=\text{Br, Cl}; \text{en}=\text{ethylendiamine}) \) and (bpy) \( \times [\text{Pt}(\text{en})\text{Br}]_2 \times [\text{ClO}_4] \times \text{H}_2\text{O} (\text{X}=\text{Br, Cl}; \text{en}=\text{ethylendiamine}) \) and (bpy) \( \times [\text{Pt}(\text{dien})\text{Br}]_2 [\text{Pt}(\text{en})\text{Br}]_2 [\text{ClO}_4] \times \text{H}_2\text{O} (\text{X}=\text{Br, Cl}; \text{en}=\text{ethylendiamine}) \) and (bpy) \( \times [\text{Pt}(\text{dien})\text{Br}]_2 [\text{Pt}(\text{en})\text{Br}]_2 [\text{ClO}_4] \times \text{H}_2\text{O} (\text{X}=\text{Br, Cl}; \text{en}=\text{ethylendiamine}) \) and (bpy) \( \times [\text{Pt}(\text{dien})\text{Br}]_2 [\text{Pt}(\text{en})\text{Br}]_2 [\text{ClO}_4] \times \text{H}_2\text{O} (\text{X}=\text{Br, Cl}; \text{en}=\text{ethylendiamine}) \) and (bpy), respectively.

II. GROUND-STATE PHASE COMPETITION

Resonant Raman spectra of \( (\text{bpy})[\text{Pt}(\text{en})\text{X}]_2 \) and \( (\text{bpy}) \times [\text{Pt}(\text{dien})\text{Br}]_2 \) both suggest a \( \text{Pt}^{2+} / \text{Pt}^{3+} (0 < \xi < 1) \) in practice valence-alternating ground state. Then, how is the interchain valence arrangement, in phase (IP) or out of phase (OP)? CDW states of the IP and OP types are indeed in close competition with varying interchain electronic communication.

Let us consider a half-filled single-band Hamiltonian, assuming the halogen \( p_x \) and ligand \( \pi \) orbitals to be fully filled and thus inactive. Here, except for the intrachain and interchain metal-to-metal supertransfers, \( t_{\text{leg}} \) and \( t_{\text{MM}} \), we use the same notation that is later defined in Eq. (3.1) and Fig. 2. The second-order perturbation scheme under the conditions of \( t_{\text{MM}} \ll t_{\text{leg}} \) gives the energies of IP- and OP-CDW states as

\[
E_{\text{IP}} = 2Ku^2 - 4\beta u + U_M + 2V_{\text{MM}}^{\text{leg}}, \tag{2.2}
\]

\[
E_{\text{OP}} = 2Ku^2 - 4\beta u + U_M + 4V_{\text{MM}}^{\text{diag}} - \frac{2(t_{\text{MM}}^{\text{leg}})^2}{4\beta u - U_M + V_{\text{MM}}^{\text{leg}} + 4(V_{\text{MM}}^{\text{diag}} - V_{\text{MM}}^{\text{diag}})}, \tag{2.3}
\]

and they are balanced at...
where \( u = |u_{n,j}| \) is the halogen-ion displacement in isolated MX chains. We show in Fig. 1 a numerical phase diagram based on Hamiltonian (2.1), which agrees well to the estimate (2.4). IP CDW and OP CDW are stabilized with increasing \( V_{MM}^{diag} \) and \( V_{MM}^{run} \) respectively. OP CDW is further stabilized with increasing \( V_{MM}^{run} \), while IP CDW has no chance of interchain electron transfer without \( \pi \) orbitals mediation (in the strongly valence-trapped limit, strictly). Nonvanishing optical absorption in the rung direction with the IP-CDW background should be significant of contributive ligand \( \pi \) orbitals.

While the ground-state phase diagram remains almost unchanged with \( p \) and/or \( \pi \) electrons taken into calculation, the single-band model totally fails to interpret the optical properties. The optical conductivity spectra measured on (bpy)(Pt(en)\(_2\))\(_2\) and (bpy)(Pt(dien)Br)\(_2\) are considerably different from each other, but it cannot distinguish between them at all. We proceed to much more elaborate calculations.

### III. MODEL HAMILTONIAN

We consider a multiband extended Peierls-Hubbard Hamiltonian of 4/5 electron filling on the two-leg ladder, 

\[
\mathcal{H} = \sum_{n,l,s} \left( \epsilon_M - \beta (u_{n,l} - u_{n-1,l}) \right) n_{n,l,M} + \epsilon_X n_{n,l,X} + \frac{\epsilon_I}{2} n_{n,l,L} \\
- \sum_{n,l,s} \left( (t_{MX} + \alpha u_{n,l}) a_{n+1,l,M}^\dagger a_{n,l,X} + (t_{XL} + \gamma a_{n,l}) a_{n+1,l,X}^\dagger a_{n,l,L} + H.c. \right) \\
+ \sum_{n,l,s,s'} \left\{ \frac{\delta_{s,s'}}{2} \sum_{A=M,X} U_A n_{n,l,A} n_{n,l,s'} + \frac{U_I}{2} n_{n,L} n_{n,L,s'} \right\} \\
+ V_{MM}^{diag}(n_{n+1,l,M} + n_{n,l,M}) n_{n,l,X} + V_{MM}^{run}(n_{n,l,X} + n_{n,l,X}) n_{n,l,L}.
\]

as is illustrated with Fig. 2, where platinum \( d_{z^2} \), halogen \( p_z \), and rung-\( \pi \) orbitals are explicitly taken into calculations. For platinum-halide single-chain compounds, typical Pt-X stretching modes are observed with frequencies of 10–40 meV and their coupling strength is estimated to be 2 to 3 eV/Å. Assuming the in-chain vibrational modes to remain valid in our ladder materials, the phonon energy is less than 1% of the optical gap \( E_{opt} \) and at most 4% of the electron-phonon interaction \( \beta \) (see Tables I and II later on). That is why we stand on the adiabatic Hamiltonian (3.1). Such a classical treatment of phonons is widely adopted and generally successful for mixed-valent platinum-halide compounds.\(^3\) Quantum phonons may be relatively effective in strongly correlated valence-delocalized nickel-halide chains.\(^4\)

Characterization of the brand new MX ladders is still in the early stage from both experimental\(^27\) and theoretical\(^3\) points of view, and therefore, little is known about the model parameters. In such circumstances, extensive two-band model studies on MX single chains serve as guides to our exploration.

Since the hopping integral \( t_{MX} \) is particularly important as an energy scale, we first set it closely consistent with the authorized estimates obtained by the Los Alamos National Laboratory working team. Comparing two-band model descriptions with first-principles local-density-approximation
calculations, they report that \( t_{\text{PCI}} = 1.54 \) eV and \( t_{\text{PBr}} = 1.30 \) eV for [Pt(en)\( _2 \)X],\(^{4,38,39}\) while \( t_{\text{PCI}} = 1.60 \) eV and \( t_{\text{PBr}} = 1.50 \) eV for [Pt(NH\( _3 \))\( _2 \)X].\(^{4,41}\) Here, we take \( t_{\text{MX}} \) to be 1.54, 1.35, and 1.32 eV for (bpy)m[Pt(en)Cl]\( _2 \), (bpy)m[Pt(en)Br]\( _2 \), and (bpy)[Pt(dien)Br]\( _2 \), respectively, considering the consistency of the resultant theoretical findings with experimental observations.

Another essential one-body parameter, the relative on-site energy \( \varepsilon_{\text{M}} - \varepsilon_{\text{X}} \), may also be less dependent on the surrounding ligands, but it is not so established as \( t_{\text{MX}} \) even in MX single chains. The Los Alamos group, on one hand, reports that \( \varepsilon_{\text{Cl}} = -1.32 \) eV and \( \varepsilon_{\text{Br}} = -0.58 \) eV for [Pt(en)\( _2 \)X].\(^{4,38,39}\) While \( \varepsilon_{\text{Cl}} = -2.90 \) eV and \( \varepsilon_{\text{Br}} = -2.30 \) eV for [Pt(NH\( _3 \))\( _2 \)X],\(^{4,41}\) but, on the other hand, suggests another possibility that \( \varepsilon_{\text{Cl}} = -4.24 \) eV and \( \varepsilon_{\text{Br}} = -1.20 \) eV for [Pt(en)\( _2 \)X],\(^{42}\) where \( \varepsilon_{\text{M}} \) is set equal to zero. Therefore, we tune the on-site energies within these estimates so as to reproduce experimental observations.

Couloymph interactions much more vary with the surrounding ligands and seriously depend on the modeling. For instance, the on-site repulsion \( U_{\text{P}} \) effectively amounts to a few eV in a pure Hubbard model,\(^{42,43}\) whereas it is strongly suppressed to a half eV or less in a fully extended model with power-law decaying Couloymph terms.\(^{44}\) Taking it into consideration that any empirical estimate of \( U_{\text{P}} \) does not exceed 2 eV,\(^{13,15,45-47}\) relying upon a well established criterion \( U_{\text{P}} \approx U_{\text{Br}} \ll U_{\text{CI}} \),\(^{4,39}\) and strictly keeping the restriction that the farther, the smaller, we compare our calculations with experimental findings on an absolute scale. The thus-obtained \( d-\rho-\pi \) model parameters for MX ladders are listed in Table I. Among the Coulouymph correlation parameters employed, \( U_{\text{A}} \) \((\text{A}=M,X,L)\) and \( V_{\text{MX}}^{\text{diag}} \) play predominant roles in reproducing the main features of the optical-conductivity spectra. The rest are much less effective for the optical properties. Indeed, we have many parameters, but their output is not so adjustable as might be expected. The effect and tuning of each parameter are further discussed and visualized in the Appendix in order to demonstrate the reliability of our parametrization.

Table II claims that our theory well interprets x-ray diffraction measurements as well as optical observations.\(^{27,28}\) Since optical conductivity of definite polarization is proportional to the relevant interatomic separation squared [see Eqs. (4.1) and (4.2)], a direct comparison of the calculations to the bare observations gives lattice constants. The Peierls gap and the lattice distortion, which are in proportion to each other, are determined within our calculation independent of any optical measurement. The optical excitation energy \( E_{\text{CT}} \) is closely related but does not coincide with the Peierls gap in the present case. The consequent lattice parameters correspond to the observations within a factor of 1.4, which guarantees our interpretation of the optical-conductivity spectra. The calculated optical gaps are also in good agreement with the observations, which justifies our parametrization. The on-site repulsion \( U_{\text{M}} \) and the site-diagonal coupling constant \( \beta \) competitively dominate \( E_{\text{CT}} \), whereas the elastic constant \( K \) is decisive of \( u \). A general tendency for halogen-ion displacements, \( u(\text{I})<u(\text{Br})<u(\text{Cl}) \), holds in MX ladders\(^{38}\) as well as in MX single chains.\(^{48}\)

### IV. OPTICAL-CONDUCTIVITY SPECTRA

#### A. Calculational procedure

In order to discuss optical absorption as a function of the polarization of incident light (\( E_{\text{in}} \)), we define current operators along ladder legs (\( l \) and rungs (\( l \times l \) as

\[
J_l = \frac{i\hbar}{c} e^{\text{MX}} \sum_{l,n,s} \left( \left( t_{\text{MX}} + au_{\text{n}} \right)a_{n+1,l,l}^\dagger a_{n,l,l} \nonumber \\
+ (t_{\text{MX}} - au_{\text{n}})a_{n,l,l}^\dagger a_{n+1,l,l} \right) + (t_{\text{XL}} - au_{\text{n}})a_{n,l,l}^\dagger a_{n+1,l,l} - \text{H.c.} \right),
\]

\[
J_l = \frac{i\hbar}{c} e^{\text{Ml}} \sum_{l,n,s} \left( -1 \right)^l \left( t_{\text{MX}} + au_{\text{n}} \right)a_{n,l,l}^\dagger a_{n+1,l,l} - \text{H.c.} \right),
\]

where \( 2e_{\text{MX}} \) and \( 2e_{\text{Ml}} \) are the intermetallic separations in the

| A | B | C | A | B | C | A | B | C | A | B | C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.98 (2.72) | 1.98 (2.73) | 0.38 (0.40) | 3.74 (3.66) | 2.00 (2.77) | 2.00 (2.74) | 0.28 (0.29) | 2.47 (2.36) | 3.50 (2.73) | 7.00 (5.59) | 0.25 (0.23) | 2.13 (2.18) |

#### B. Table II. Theoretical (bare) and experimental (inside parentheses) estimates of structural and optical parameters for (A) (bpy)m[Pt(en)Cl]\( _2 \), (B) (bpy)m[Pt(en)Br]\( _2 \), and (C) (bpy)[Pt(dien)Br]\( _2 \) for the Pt-X-Pt and Pt-L-Pt distances, respectively, while \( u \) to the X displacement from the mid point. \( E_{\text{CT}} \) is the intrachain charge-transfer excitation energy.

235116-3
Then, the real part of the optical conductivity reads

\[
\sigma_{\text{LL}}(\omega) = \frac{\pi}{\omega} \sum_i |E_i| J_{\text{LL}} |E_0| |^2 \delta(E_i - E_0 - \hbar \omega),
\]

where \( |E_i| \) is the \( i \)th-lying state of energy \( E_i \). \( |E_0| \) is defined as

\[
|E_0| = \prod_{\epsilon_\mu < \epsilon_F} c_{\mu s}^\dagger c_{\mu s} |0\rangle,
\]

where \(|0\rangle\) is the true electron vacuum, \( \epsilon_F \) is the Fermi energy, and \( c_{\mu s}^\dagger \) creates an electron of spin \( s \) in the Hartree-Fock (HF) eigenstate with an eigenvalue \( \epsilon_{\mu s} \). Excited states are calculated within and beyond the HF scheme, being generally defined as

\[
|E_i\rangle = \sum_{\epsilon_{\mu s} < \epsilon_F} f(\mu, \nu, s; i) c_{\nu s}^\dagger c_{\mu s} |E_0\rangle.
\]

Every excited state of the HF type is a single Slater determinant, where \( f(\mu, \nu, s; i) = \delta_{\mu \nu, s} \). Those of the configuration-interaction (CI) type consist of resonating Slater determinants, where \( f(\mu, \nu, s; i) \) satisfies

\[
\sum_{\epsilon_{\mu s} < \epsilon_F} \langle E_0| c_{\mu s}^\dagger c_{\nu s'} | \mathcal{H} c_{\nu s'} c_{\mu s} | E_0 \rangle f(\mu, \nu, s; i) = E_i f(\mu', \nu', s'; i),
\]

that is, the unitary matrix \( f(\mu, \nu, s; i) \) diagonalizes the original Hamiltonian \( \mathcal{H} \). Since the HF Hamiltonian \( \mathcal{H}_{\text{HF}} \) is diagonal with respect to pure particle-hole states as \( \langle E_0| c_{\mu s}^\dagger c_{\nu s'} | \mathcal{H}_{\text{HF}} c_{\nu s'} c_{\mu s} | E_0 \rangle = \delta_{\mu \nu} \delta_{s s'} (E_0 - \epsilon_{\mu s} + \epsilon_{\nu s'}) \), the residual component \( \mathcal{H} - \mathcal{H}_{\text{HF}} \) mixes the Slater determinants and reduces the interband transition energy (see Figs. 4 and 5 later). Equation (4.3) calculated is Lorentzian broadened.

**B. Single-band calculation**

Before analyzing experimental findings in detail, we calculate the optical conductivity in terms of the single-band Hamiltonian (2.1) in an attempt to demonstrate the indispensable halogen \( p_s \) and ligand \( \pi \) orbitals. Figure 3 shows that the optical observations of IP- and OP-CDW states are quite alike without contributive \( p \) and \( \sigma \) electrons. The spectra in the leg direction are single peaked, whereas no significant spectral weight lies in the rung direction.

![Image](image-url)
However, the lowest- and highest-energy ones are optically forbidden and the rest, optically allowed, cost the same energy. The conduction and filled bands are exactly symmetric with respect to the Fermi level due to the electron-hole symmetry preserved. That is why not only the OP-CDW spectrum but also the IP-CDW spectrum is single peaked. The single-peak structure remains unchanged with excitonic effect on. A consideration of $X \rho_z$ and/or $L \pi$ orbitals leads to the breakdown of the electron-hole symmetry and lifts the degeneracy between the optical observations of IP CDW and OP CDW, which is essential to the understanding of experimental findings.

The vanishing weight of $\sigma_s(\omega)$ is also due to the sleeping $p$ and $\pi$ electrons and is never in agreement with any experiment. We are thus lead to the $d$-$p$-$\pi$ modeling.

### C. $d$-$p$-$\pi$ description

In Figs. 4 and 5, we compare the $d$-$p$-$\pi$ calculations of the optical conductivity with experimental observations,$^{28}$ that is, the Kramers-Kronig transforms of polarized reflectivity spectra for the single crystals at room temperature. The calculations qualitatively interpret most of the spectral features within the HF scheme and quantitatively improves with excitonic effects. We have two arguments, in particular: (i) For $E_{in} \parallel \varepsilon$, the main absorption band is double peaked in (bpym)[Pt(en)X]$_2$, but single peaked in (bpym)[Pt(dien)Br]$_2$.

![Graph](image)

**FIG. 6.** (Color online) Hartree-Fock calculations of the dispersion relation $\epsilon_k$ and the local (total) density of states $\rho(\epsilon)$ [$\rho(\epsilon) = \sum_{n,LA} \rho_{n,LA}(\epsilon)$] for (a) IP-CDW and (b) OP-CDW states describing (bpym)[Pt(en)Cl]$_2$ and (bpym)[Pt(dien)Br]$_2$, respectively. Major optical absorptions with $E_{in} \parallel \varepsilon$ and $E_{in} \perp \varepsilon$ are indicated by solid and dotted arrows, respectively, in Figs. 4 and 5 as well as here.
allowed excitations of two types. Thus, we find a double-electron-hole symmetry that unequalizes the optically allowed excitations.

**V. SUMMARY**

(bpy)[Pt(en)X]$_2$ reveal themselves as $d$-$p$-$\pi$-hybridized multiband ladder materials with a ground state of the IP-CDW state and is strengthened, roughly doubled, in an OP-CDW state. However, it is still much less recognizable than that in the leg direction. Most of the spectral weight is distributed to the higher-energy region, which is attributable to $\pi$-$d$ charge-transfer excitations. The single-excitation CI scheme seems still incomplete but fully demonstrates the crucial role of electronic correlations in reproducing the observations quantitatively. It may also be effective to take ligand $\pi^\ast$ orbitals into calculation. Here, we have discarded the vacant $\pi^\ast$ orbitals, on one hand, assuming them to be higher lying than $d_{z^2}$ orbitals and, on the other hand, avoiding further increase of the number of parameters. A pioneering density-functional study on (bpy)[Pt(en)Cl]$_2$ proposes a level scheme of the bpy $\pi^\ast$ orbitals being sandwiched between the $d_{z^2}$(Pt$^{4+}$) and $d_{z^2}$(Pt$^{4+}$) bands. Such a scenario looks consistent with our underestimation of $\sigma_{\Omega}(\omega)$ for (bpy)[Pt(en)X]$_2$ and may explain the low-energy shoulder or foot of its widespread band. On the other hand, the bpy $\pi^\ast$ orbitals are likely to lie above the Pt $d_{z^2}$ bands, judging from Fig. 5.
OPTICAL CHARACTERIZATION OF PLATINUM-HALIDE...

CDW type, while (bpy)[Pt(dien)Br]_2 as a d_{2z}-single-band double-chain material with a ground state of the OP-CDW type, which is reminiscent of conventional MX chain compounds. The two ground states are highly competitive and both materials sit in the vicinity of the phase boundary. An iodine derivative of the former compounds, (μ-bpym)\[\text{[Pt(en)Cl]}_2\]_2, might have a ground state of OP-CDW, which is also stabilizes a site-diagonal CDW, providing a dotted line of the polarized optical-conductivity spectra parallel to ladder legs for IP-CDW states in comparison with an experimental observation (a dotted line) of (bpym)[Pt(en)Cl]_2, where all the parameters but \(V_{\text{leg}}^{\text{MX}}\) are fixed at set A in Table I.

There lie ahead fascinating topics such as quantum phase transitions and nonlinear photoproducts in this geometrically designed Peierls-Hubbard multiband system. Palladium and nickel analogs as well as ligand substitution will contribute toward realizing further density-wave states possible in a multiorbital ladder lattice. Photogenerated excitons and their relaxation channels were extensively calculated for MX (Refs. 1, 2, 51, and 52) and MMX (Refs. 53 and 54) chains, and the predicted scenarios were indeed demonstrated experimentally.\(^{48,55}\) Photoexcited MX ladders are more and more interesting. Contrastive materials with IP-CDW and OP-CDW backgrounds have been provided and identified. The next stage is ready for further investigations.

ACKNOWLEDGMENTS

We are grateful to K. Iwano for fruitful discussions and valuable comments on our calculation. H. Matsuzaki and H. Okamoto have allowed and encouraged us to discuss their elaborate optical observations. Their kindness is greatly appreciated. We further thank D. Kawakami, M. Yamashita, A. Kobayashi, and H. Kitagawa for useful information on their brand-new MX ladder products. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

APPENDIX: ON THE PARAMETER TUNING

We have reached the best solutions in Figs. 4 and 5 systematically tuning all the parameters. The optical-conductivity spectral shape monotonically varies as we tune each parameter. We demonstrate the parameter tuning for (bpym)[Pt(en)Cl]_2 and discuss what roles leading parameters play in reproducing the spectra.

Varying \(U_M\) slides, rather than deform, the spectrum (Fig. 7). With increasing \(U_M\), the Peierls gap is reduced and any charge-transfer excitation energy monotonically decreases. The effect of electron-lattice interactions can be understood in the same context. The site-diagonal coupling constant \(\beta\) straightforwardly stabilizes a CDW on metal sites. Considering M-X charge-transfer energy gains, the site-off-diagonal coupling constant \(\alpha\) also stabilizes a site-diagonal CDW rather than a site-off-diagonal (bond-centered) CDW, provided \(\epsilon_M \neq \epsilon_X\). Both \(\alpha\) and \(\beta\) work against \(U_M\). All these parameters position the intrachain charge-transfer band.

\(U_X\) and \(\epsilon_X\) adjust the spectral weight of the main absorption band originating from intrachain M-X charge transfer excitations (Fig. 8). The oscillator strength of the charge-transfer band increases with activated \(\nu\) electrons. Increasing \(U_X\) induces oxidation of \(X^+\) ions, while \(\epsilon_X\) approaching to \(\epsilon_M\) activates \(d-p\) hybridization. The spectral weight increases with increasing \(U_X\) and decreasing \(\epsilon_M - \epsilon_X\).

Parameters related to rung ligands control the structure of the main absorption band (Fig. 9). With increasing \(U_L\), \(\epsilon_L\) approaching to \(\epsilon_M\) and increasing \(t_{ML}\), \(d-\pi\) hybridization is encouraged. Then, the intrachain \(d\) bands of Pt^{2+} character split into their bonding and antibonding combinations, and the charge-transfer band is doubly peaked.
Finally we take a look at the effect of different-site Coulomb interactions (Fig. 10). The HF decomposition of any Coulomb term reminds us that the Coulomb interaction originates from electron hopping between the relevant sites. \( V_{\text{MX}} \) indeed modulates the band gap in the same way as \( \alpha \) at the HF level. However, the configuration interaction restructures the charge-transfer band and drastically changes its double-peaked features. With \( V_{\text{MX}} \) large enough, the lower-energy absorption can even be stronger than the higher-energy one. \( V_{\text{diag}} \) and \( V_{\text{diag}} \) are also important Coulomb interactions, though they act on the next-nearest-neighbor sites. They highly compete with each other for the ground-state valence arrangement. Therefore, these parameters are much less tunable and determined with smaller uncertainty. Thus, we are led to the parametrization in Table I and theoretical findings in Figs. 4 and 5. Considering the structural data as well, there is no better solution within the present modeling.

1 A. Mishima and K. Nasu, Phys. Rev. B 39, 5758 (1989).
2 A. Mishima and K. Nasu, Phys. Rev. B 39, 5763 (1989).
3 J. T. Gammel, A. Saxena, I. Batistić, A. R. Bishop, and S. R. Phillpot, Phys. Rev. B 45, 6408 (1992).
4 S. M. Weber-Milbrodt, M. A. Stroud, S. D. Conradson, and M. H. Zietlow, Bull. Chem. Soc. Jpn. 66, 2406 (1993).
5 S. Yamamoto, J. Phys. Chem. Solids 63, 125124 (2001).
6 M. Kuwabara and K. Yonemitsu, J. Mater. Chem. 11, 2163 (2001).
7 B. I. Swanson, M. A. Stroud, S. D. Conradson, and M. H. Zietlow, Sol. State Commun. 65, 1405 (1988).
8 S. Yamamoto, Phys. Rev. B 64, 140102(R) (2001).
9 S. Yamamoto, J. Phys. Chem. Solids 63, 1489 (2002).
10 H. Matsuzaki, T. Matsuoka, H. Kishida, K. Takizawa, H. Miyasaka, K. Sugijura, M. Yamashita, and H. Okamoto, Phys. Rev. Lett. 90, 046401 (2003).
11 K. Yonemitsu and N. Miyashita, Phys. Rev. B 68, 075113 (2003).
12 H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukuda, T. Matani, M. Seto, and Y. Maeda, J. Am. Chem. Soc. 121, 10068 (1999).
13 S. Yamamoto, J. Phys. Soc. Jpn. 70, 1198 (2001).
14 K. Sakai, Y. Tanaka, Y. Tsuchiya, K. Hirata, T. Tsubomura, S. Iijima, and A. Bhattacherjee, J. Am. Chem. Soc. 120, 8366 (1998).
15 J. Yi, T. Miyabayashi, M. Ohashi, T. Yamagata, and K. Kishida, Inorg. Chem. 43, 6596 (2004).
16 A. Kobayashi and H. Kitagawa, J. Am. Chem. Soc. 128, 12066 (2006).
17 D. Kawakami, M. Yamashita, S. Matsunaga, S. Takaiishi, T. Kajiwara, H. Miyasaka, K. Sugijura, H. Matsuzaki, and H. Okamoto, Angew. Chem. 118, 7372 (2006).
18 S. Nishimoto, E. Jeckelmann, and D. J. Scalapino, Phys. Rev. B 66, 245109 (2002).
19 M. Aichhorn, M. Hohenadler, E. Ya. Sherman, J. Spitaler, C. Ambrosch-Draxl, and H. G. Evertz, Phys. Rev. B 69, 245108 (2004).
20 K. Funase and S. Yamamoto, J. Phys. Soc. Jpn. 75, 044717 (2006).
21 L. Degiorgi, P. Wachtner, M. Haruki, and S. Kurita, Phys. Rev. B 40, 3285 (1989).
22 K. Nasu, Phys. Rev. B 52, 3865 (1993).
23 D. Baeriswyl and A. R. Bishop, J. Phys. C 21, 339 (1988).
24 Y. Tagawa and N. Suzuki, J. Phys. Soc. Jpn. 64, 1800 (1995).
25 S. Yamamoto, Phys. Rev. B 66, 165113 (2002).
26 K. Iwano and Y. Shimoj, J. Phys. Soc. Jpn. 76, 063708 (2007).
27 R. C. Albers, Synth. Met. 29, 169 (1989).
28 R. C. Albers, M. Alouani, J. M. Wills, and M. Springborg, Synth. Met. 42, 2739 (1991).
29 M. Alouani, R. C. Albers, J. M. Wills, and M. Springborg, Phys. Rev. Lett. 69, 3104 (1992).
30 M. Alouani, J. W. Wilkins, R. C. Albers, and J. M. Wills, Phys. Rev. Lett. 71, 1415 (1993).
31 A. Saxena, Z. Shuai, J. T. Gammel, I. Batistić, M. Alouani, J. L. Brédas, and A. R. Bishop, Synth. Met. 71, 1659 (1995).
32 S. D. Conradson, M. A. Stroud, M. H. Zietlow, B. I. Swanson, D. Baeriswyl, and A. R. Bishop, Solid State Commun. 65, 723 (1988).
33 I. Batistić, X. Z. Huang, A. R. Bishop, and A. Saxena, Phys. Rev. B 48, 6065 (1993).
34 S. Kurita, M. Haruki, and K. Miyagawa, J. Phys. Soc. Jpn. 57, 1789 (1988).
35 Y. Wada, T. Mitani, K. Toriumi, and M. Yamashita, J. Phys. Soc. Jpn. 58, 3013 (1989).
36 M. Sakai, N. Kuroda, and Y. Nishina, Phys. Rev. B 40, 3066 (1989).
37 H. Okamoto and M. Yamashita, Bull. Chem. Soc. Jpn. 71, 2023 (1998).
38 Y. Wada, T. Mitani, M. Yamashita, and T. Koda, J. Phys. Soc. Jpn. 54, 3143 (1985).
39 D. Kawakami and M. Yamashita (private communication).
40 M. Suzuki and K. Nasu, Phys. Rev. B 45, 1605 (1992).
41 K. Iwano, J. Phys. Soc. Jpn. 66, 1088 (1997).
42 J. Ohara and S. Yamamoto, J. Phys. Soc. Jpn. 74, 250 (2005).
43 J. Ohara and S. Yamamoto, Phys. Rev. B 73, 045122 (2006).
44 H. Tanaka, S. Kuroda, T. Yamashita, M. Mitsumi, and K. Toriumi, J. Phys. Soc. Jpn. 72, 2169 (2003).