Photoproduction of spin and charge carriers in halogen-bridged binuclear platinum chain complexes

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Abstract
Nonlinear lattice relaxation of photoexcited diplatinum-halide chain compounds is theoretically investigated within a one-dimensional extended Peierls–Hubbard model. We first illuminate the whole relaxation scenario in terms of variational wavefunctions and then visualize each story as a solution of the Schrödinger equation. Neutral solitons and/or polarons were observed in conventional platinum-halide chains, and they are highly resonant on the occasion of their birth and geminate recombination.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Halogen (X)-bridged binuclear transition-metal (M) linear-chain complexes [1–4] have stimulated a renewed interest in the MX class of materials [5, 6]. Metal binucleation induces an unpaired electron per metal-dimer unit even in valence-trapped states, contrasting with the Peierls-gapped state of M$^2$+ and M$^+$ in conventional MX chains. The Md$\cdots$Md$\cdots$ direct overlap effectively reduces the on-site Coulomb repulsion due to its $d_{z^2}$ character, remarkably enhancing the electron itinerancy. The MMX electronic state is thus activated and full of variety [7, 8]. Diplatinum-halide varieties, A$_2$[Pt$_2$(pop)$_2$X]$m$H$_2$O (X = Cl, Br, I; A = NH$_4$, Na, K, …; pop = diphosphonate = $P_2$O$_5$H$_2$) [1, 2] structurally resemble conventional MX compounds and exhibit the most likely charge density wave (CDW) with the halogen-sublattice dimerized [9, 10]: $\cdots$X$^-\cdots$Pt$^{2+}$Pt$^{2+}$X$^-\cdots$X$^-\cdots$Pt$^{2+}$Pt$^{2+}$X$^-\cdots$. However, the ground state is quite sensitive to bridging halogens and counter ions [11, 12]. In the iodo complexes the valence arrangement is highly tunable with pressure application and optical irradiation [13–18]. Their analogue without any counter ion, Pt$_3$(dta)$_2$I (dta = dithioacetate = CH$_2$CS$_2$) [3], is of metallic conduction above room temperature [19, 20]. With decreasing temperature, it undergoes successive phase transitions [21–24] and ends up with a distinct Peierls-distorted state of alternating charge polarization (ACP) [25, 26]: $\cdots$I$^-\cdots$Pt$^{2+}$Pt$^{3+}$I$^-\cdots$Pt$^{2+}$Pt$^{2+}$I$^-\cdots$. Where the metal sublattice, which is free from any hydrogen bonding, is dimerized. The methyl group in the dta ligand can be replaced by longer alkyl chains [27, 28]. There indeed appear new vibrational features in the resonant Raman spectra of K$_4$[Pt$_2$(pop)$_2$Cl]$m$H$_2$O, which can be ascribed to polaronic defects due to the deficiency of counter ions [37]. Electron-spin-resonance (ESR) measurements on Pt$_3$(C$_4$H$_7$I$_2$) reveal thermally activated mobile spins attributable to neutral solitons [38]. Photoexcitation is a promising approach to producing these valence anomalies in a systematic fashion. Thus motivated, we analyse the electron–lattice dynamics of photoexcited Pt$_2$X chains. We first reveal the whole relaxation scenario in terms of variational wavefunctions and then visualize each story as a solution of the Schrödinger equation. Neutral solitons and/or polarons were observed in [Pt(en)$_2$Cl](ClO$_4$)$_2$ (en = ethylenediamine =
C$_2$H$_4$N$_2$) [39–41], whereas charged solitons and polarons were in [Pt(en)$_2$I](ClO$_4$)$_2$ [42, 43]. However, neutral and charged solitons do not seem able to coexist as photoproducts in any MX chain [32, 44]. There may be a wider variety of relaxation channels in varied MMX chains [45].

2. Modelling

We describe Pt$_2$X chains by the $\frac{1}{2}$-filled single-band Peierls–Hubbard Hamiltonian

$$\mathcal{H} = -\sum_{n,s} [t_{\text{MM}} - \alpha(l_{n+1} + r_n)] (a_{n+1,s}^\dagger b_{n,s} + b_{n,s}^\dagger a_{n+1,s})$$

$$- t_{\text{MM}} \sum_{n,s} (b_{n,s}^\dagger a_{n,s} + a_{n,s}^\dagger b_{n,s})$$

$$- \beta \sum_{n,s} (l_n n_{n,s} + r_n m_{n,s}) + \frac{K_{\text{MX}}}{2} \sum_n (t_n^2 + r_n^2)$$

$$+ \frac{M_X}{2} \sum_n a_n^2 + M_M \sum_n a_n^2$$

$$+ U_M \sum_n (n_{n,\uparrow} n_{n,\downarrow} + m_{n,\uparrow} m_{n,\downarrow})$$

$$+ \sum_{n,s,s',t} (V_{\text{MM}} n_{n,s} n_{n,s'} + V_{\text{MX}} n_{n+1,s} m_{n,s'}),$$

(2.1)

where $n_{n,s} = a_{n,s}^\dagger a_{n,s}$ and $m_{n,s} = b_{n,s}^\dagger b_{n,s}$ with $a_{n,s}^\dagger$ and $b_{n,s}^\dagger$ creating an electron with spin $s = \uparrow, \downarrow \pm$ on the Pt$d_{5z}$ orbitals in the nth diplatinum unit. $t_{\text{MM}}$ and $t_{\text{MX}}$ describe the intradimer electron transfer and the interdimer electron supertransfer, respectively, and are set for $t_{\text{MM}} = 2t_{\text{MX}}$. $\alpha$ and $\beta$ characterize electron–lattice interactions of the Peierls and Holstein types, respectively. $l_n = v_n - u_{n-1}$ and $r_n = u_n - v_n$, with $u_n$ and $v_n$ being, respectively, the chain-direction displacements of the nth halogen ion and diplatinum cluster from their equilibrium positions. Deformation of every diplatinum cluster is negligible. $K_{\text{MX}}$ is the platinum–halogen spring constant, while $M_X$ and $2M_M$ are the masses of a halogen atom and a diplatinum complex, respectively. Any calculation is carried out in a chain of a hundred or more Pt$_2$X units under the periodic boundary condition, where no significant size effect survives.

We show in figure 1 a ground-state phase diagram of the Hamiltonian (2.1) within the Hartree–Fock (HF) approximation. The site-diagonal Holstein-type electron–lattice coupling stabilizes the CDW state against the Mott–Hubbard (MH) insulating state, while the site-off-diagonal Peierls-type one contributes towards realizing the ACP state. We consider both pop and dta families of Pt$_2$X complexes, setting $(\alpha, \beta)/\sqrt{t_{\text{MX}}K_{\text{MX}}}$ equal to (0.0, 1.2) and (0.3, 0.8), respectively. Typical PtX chains lie in the intermediate-correlation regime [6, 32] of $V_{\text{MX}} \ll U_M \approx t_{\text{MX}}$ and platinum binucleation should effectively reduce the onsite repulsion. Thus we fix the PtX Coulomb parameters at $(U_M, V_{\text{MM}}, V_{\text{MX}})/t_{\text{MX}} = (0.5, 0.25, 0.15)$. The d–p hybridization and the resultant interdimer supertransfer significantly depend on the bridging halogens. The Pt–I transfer integral is indeed a few times as large as the Pt–Cl one [37, 46]. The present parametrization well features PtX chains, but the Coulomb parameters, when scaled, may fundamentally vary with X.

3. Variational calculation

Photoinduced charge-transfer excitations first spread over the chain and then transform themselves into local defects. Such self-localization processes can be visualized through the calculation of adiabatic potential energy surfaces in a variational manner [32, 33, 44, 45]. Solitonic relaxation channels are describable with a trial wavefunction

$$l_n = \sigma (-1)^n \alpha \left[ 1 + \kappa \left( \tanh \frac{|n| - d/2}{\xi} - 1 \right) \right],$$

(3.1)

whereas polaronic ones with

$$l_n = \sigma (-1)^n \alpha \left[ 1 + \kappa \left( \tanh \frac{|n| + \delta - d/2}{\xi} - 1 \right) \right],$$

(3.2)

where the variational parameters $\kappa$, $\xi$, and $\delta$ are determined at every interdimer distance $d$ given so as to minimize the energy of the lowest-lying excited state, setting $\lambda$ equal to the uniform halogen-ion displacement relative to neighbouring diplatinum clusters in the CDW ($\sigma = 1$) or ACP ($\sigma = -1$) ground state. Once the ground state is photoexcited into the Frank–Condor state, which still sits at $\kappa = 0$, the uniform bond alternation begins to locally deformed. Increasing $\kappa$ with $d$ remaining to be zero depicts the self-stabilization of a charge-transfer exciton. The fully stabilized, that is to say, self-trapped exciton (STE) may have paths to a pair of solitons and antisolitons and that of polarons. Such defect pairs may be directly generated from free electron–hole pairs, which are higher-lying excited states, with $\kappa$ and $\delta$ being tuned simultaneously. $\xi$ determines the width of a defect. $\delta$ is just a minor parameter, bringing the defect centre any other types of valence oscillation besides the ground-state one [36].

![Figure 1. Hartree–Fock calculation of a ground-state phase diagram on the $\alpha$-U_M cube for MMX chains.](image-url)
The lattice configuration is adiabatically determined within the HF scheme. The ground-state bond-alternation amplitude \( \lambda \) minimizes \( E_0|\mathcal{H}|E_0^t \equiv E_0^t \) in a chain of constant length, where

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

with \(|0\rangle\) denoting the true electron vacuum, \( \epsilon_F \) indicating the Fermi energy and \( c_{\mu,s}^\dagger \), generally given as \( \sum_{\rho}(d_{\mu,s,\rho}a_{\mu,s,\rho}^\dagger + \psi_{\mu,s,\rho}^\dagger b_{\mu,s,\rho}) \), creating an electron of spin \( s \) in the HF eigenstate of eigenvalue \( \epsilon_{\mu,s} \). The excited-state parameters \( \kappa, \xi \) and \( \delta \) minimize \( E_1^t|\mathcal{H}|E_1^t|HF, \) where

\[
|E_1^t| = c_{\mu,s}^\dagger c_{\mu,s}^\dagger |E_0^t|,
\]

provided \( \epsilon_{\mu,s} < \epsilon_F < \epsilon_{\nu,s} \). For the first excited state \( l = 1 \), \( \mu \) and \( \nu \) are set equal to the highest-lying occupied and lowest-lying vacant levels, respectively. When we take particular interest in the \( l \)th energy surface, \( E_1^t|\mathcal{H}|E_1^t|HF \) may be minimized instead. However, the whole energy scheme is not so sensitive to the variational target as to be qualitatively changeable. In any case the HF \( l \)th excited-state energy \( E_{lHF}^t \) is trivially written as \( E_0^t + \epsilon_{\nu,s} - \epsilon_{\mu,s} \).

We further consider configuration interactions (CIs) between the HF excited states in an attempt to describe Coulomb correlations with more precision. Excited states of the single-particle–hole CI type are expressed as

\[
|E_l^CI| = \sum_{\epsilon_{\nu,s}<\epsilon_{\mu,s}} f(\mu, \nu, s; l)c_{\nu,s}^\dagger c_{\mu,s}^\dagger |E_0^t|,
\]

where \( f(\mu, \nu, s; l) \) diagonalizes the original Hamiltonian (2.1). The refined \( l \)th excited-state energy \( E_{lCI}^t \) is given by \( c_l(E_l)|\mathcal{H}|E_l|CFI, \) where \( E_{lCI}^t \) is plotted by solid lines, while \( E_{lHF}^t \) by symbols. A fully stabilized exciton, unless it decays by luminescence, may be dissociated into a neutral (1) or charged (2) soliton (\( S \)-antisoliton (\( \bar{S} \)) pair. Any potential soliton pair is so fragile as to recombine and disappear (3). Polaron (\( P \)) pairs may be generated by high-energy excitations reaching the electron–hole continuum.

Figure 2 presents the thus-calculated adiabatic potential energy surfaces of point-like photoexcited Pt\(_2\)X chains whose ground states are of the CDW (a) and ACP (b) types, which are relevant to A\(_i\)Pt\(_2\)(pop)_4X\(_4\)H\(_2\)O and Pt\(_2\)(dta)_4I\(_4\), respectively. \( E_{lHF}^t \) is plotted.

4. Real-time dynamics

We trace charge-transfer excitations as functions of real time solving of the Schrödinger equation:

\[
i\hbar \dot{\Psi}_{\mu,s}(t) = H_{lHF}^t(t)\Psi_{\mu,s}(t),
\]

where \( H_{lHF}^t(t) \) and \( \Psi_{\mu,s}(t) \), the spin-\( S \) sectors of the HF Hamiltonian and wavefunction, are given by a square matrix and a column vector of degree \( 2N \), respectively. Defining the
wavevector as

$$\Psi_{\mu,i}(t) = \begin{bmatrix}
\dot{\varphi}_{\mu,1,i}(t) \\
\dot{\varphi}_{\mu,2,i}(t) \\
\vdots \\
\dot{\varphi}_{\mu,N,1,i}(t) \\
\varphi_{\mu,N,2,i}(t)
\end{bmatrix}, \quad (4.42)$$

and employing a unitary transformation

$$U = \begin{bmatrix}
0 & 1 & 0 & \cdots & 0 \\
0 & 0 & 1 & \ddots & \vdots \\
\vdots & \ddots & \ddots & \ddots & 0 \\
0 & \cdots & 0 & 0 & 1 \\
1 & 0 & \cdots & 0 & 0
\end{bmatrix}, \quad (4.33)$$

we express the Hamiltonian as

$$H_{HF}^U(t) = \begin{bmatrix} \mathcal{P}_{\mu,1}(t), \ldots, \mathcal{P}_{N}(t) \end{bmatrix} + U^† \begin{bmatrix} \mathcal{Q}_{\mu,1}(t), \ldots, \mathcal{Q}_{N}(t) \end{bmatrix} U,$$

where the $2 \times 2$ matrices

$$\mathcal{P}_{\mu,1}(t) = \begin{bmatrix}
-\frac{\hbar}{2}[\mu(t) - \nu_{n-1}(t)] \\
+\frac{\hbar}{2}A_{n-1}(t) \\
+\frac{\hbar}{2}B_{n-1}(t) \\
-\hbar\Delta M - V_{MM} P_{\mu,1}(t)
\end{bmatrix},$$

$$\mathcal{Q}_{\mu,1}(t) = \begin{bmatrix}
-\frac{\hbar}{2}[\nu_{n}(t) - \nu_{n}(t)] \\
+\frac{\hbar}{2}A_{n-1}(t) \\
+\frac{\hbar}{2}B_{n-1}(t) \\
-\hbar\Delta M - V_{MM} Q_{\mu,1}(t)
\end{bmatrix},$$

are self-consistently calculated through

$$A_{\mu}(t) = \sum_{s} A_{\mu,s}(t) = \sum_{s} \sum_{\mu} \left| \varphi_{\mu,s,i}(t) \right|^2,$$

$$B_{\mu}(t) = \sum_{s} B_{\mu,s}(t) = \sum_{s} \sum_{\mu} \left| \dot{\varphi}_{\mu,s,i}(t) \right|^2,$$

$$P_{\mu}(t) = \sum_{s} P_{\mu,s}(t) = \sum_{s} \sum_{\mu} \dot{\varphi}_{\mu,s,i}(t) \varphi_{\mu,s,i}(t),$$

$$Q_{\mu}(t) = \sum_{s} Q_{\mu,s}(t) = \sum_{s} \sum_{\mu} \dot{\varphi}_{\mu,s,i}(t) \varphi_{\mu,s+1,i}(t),$$

with $\sum$ denoting the summation over the initially occupied levels. Now the HF wavevector $\{\varphi_{\mu,s,i}, \dot{\varphi}_{\mu,s,i}(t)\}$ and the lattice configuration $\{\nu_{n}, \nu_{n}(t)\}$ are both time-dependent. Discretizing the time variable as $t_j = j\Delta t$ ($j = 0, 1, 2, \ldots$) with the interval $\Delta t$ much smaller than $\omega^{-1}$, we schematically integrate equation (4.42):

$$\Psi_{\mu,i}(t_{j+1}) = \hat{T} \exp \left[ -\frac{i}{\hbar} \int_{t_j}^{t_{j+1}} H_{HF}^U(t) \, dt \right] \Psi_{\mu,i}(t_j), \quad (4.47)$$

where $\hat{T}$ denotes the time ordering. Employing a general decomposition theory of ordered exponentials [48], together with the expression (4.44), we can carry out the time evolution of equation (4.7) without numerically diagonalizing $H_{HF}^U(t)$ at every time step [49], which serves to accelerate the calculation. We adopt a fractal decomposition up to the third order of $\Delta t$ [50, 51].

The lattice dynamics is governed by Newton’s equation of motion:

$$M_N \ddot{u}_n(t) = K_M \nu_{n+1}(t) - 2u_n(t) + V_n(t),$$

$$\beta[A_{n+1}(t) - B_n(t)] = F_n(t),$$

$$2M_M \ddot{v}_n(t) = K_M [u_{n+1}(t) - 2u_n(t) + u_{n-1}(t)],$$

$$\beta[A_n(t) - B_n(t)] + \alpha [P_n(t) + Q_n^*(t)] - Q_{n-1}(t) = G_n(t).$$

With the discrete time variable, we evolve the lattice configuration as

$$u_n(t_{j+1}) = u_n(t_j) + \dot{u}_n(t_j) \Delta t,$$

$$\ddot{u}_n(t_{j+1}) = \ddot{u}_n(t_j) + \frac{F_n(t_j)}{M_N} \Delta t,$$

$$\ddot{v}_n(t_{j+1}) = v_n(t_j) + \ddot{v}_n(t_j) \Delta t,$$

$$\ddot{\nu}_n(t_{j+1}) = \dot{\nu}_n(t_j) + \frac{G_n(t_j)}{2M_M} \Delta t.$$

We start any calculation from a stationary lattice of the CDW or ACP type:

$$v_n(t_0) = u_{n-1}(t_0) = \sigma (-1)^n \lambda + \Delta l_n(t_0),$$

$$u_n(t_0) - v_n(t_0) = (-1)^n \lambda + c(t_0),$$

$$\dot{\nu}_n(t_0) = \dot{\nu}_n(t_0) = 0,$$

where $\Delta l_n(t_0), \Delta c(t_0)$ are introduced at random as thermal fluctuations.

In an attempt to guide future experiments, we adopt a realistic set of parameters: $t_{\Delta M} = 1.5 \text{ eV}$, $K_{\Delta M} = 8.0 \text{ eV} \hbar^{-1}$, $2M_M = 13.4 \times 10^5 M_e$ and $M_N = 2.3 \times 10^6 M_e$ [35, 36], where $M_e$ is the electron mass. Numerical integration is reliable enough with $\Delta t = 10^{-3} \omega^{-1} \approx 0.0255$ fs. The initial disorder ($\Delta l_n(t_0), \Delta c(t_0)$) is restricted to $10^{-4} \lambda$, which corresponds to the temperatures $10^4 \lesssim T \lesssim 0.05 \hbar/\omega \lesssim 20 K$, where both CDW and ACP ground states are fully stabilized [13, 21].

We first pump an electron to the first excited state and observe the following time evolution. Typical examples are shown in figures 3 and 4. Photoproduction of neutral (1) and charged (2) soliton–antisoliton pairs and their ginate recombination in the early stage (3) are clearly found on both
Figure 3. Contour plots of bond, spin and charge variables as functions of space and time for the first excited state of a Pt$_2$X chain with a CDW ($\sigma = 1$) background: (a) the bond order parameters $\tilde{t}_n(t) = \sigma (-1)^n [-I_{n-1}(t) + 2I_n(t) - I_{n+1}(t)]/4$, $r_n(t) = (-1)^n [-r_{n-1}(t) + 2r_n(t) - r_{n+1}(t)]/4$; (b) twice the net spin densities $\tilde{S}_n(t) = \sum_s \tilde{A}^{(1)}_{n,s}(t)$, $\tilde{T}_n(t) = \sum_s \tilde{B}^{(1)}_{n,s}(t)$; where $I_n(t) = v_n(t) - u_{n-1}(t)$ and $r_n(t) = u_n(t) - v_{n+1}(t)$, while $A^{(1)}_{n,s}(t) = \sum_\mu f^{(1)}_{\mu,s}(\theta_\mu,\epsilon_n(t))^2$ and $B^{(1)}_{n,s}(t) = \sum_\mu f^{(1)}_{\mu,s}(\varphi_\mu,\epsilon_n(t))^2$ with $f^{(1)}_{\mu,s}$ being the time-independent distribution function of spin-$s$ electrons for the $l$th excited state. When $l = 1$, $f^{(1)}_{\mu,s} = 1$ for $\mu \leq 3N/2$ and $f^{(1)}_{\mu,s} = 0$ for $\mu > 3N/2$ but $f^{(1)}_{3N/2,\uparrow} = 0$ and $f^{(1)}_{3N/2+1,\uparrow} = 1$.

Figure 4. The same as figure 3 but with an ACP ($\sigma = -1$) background.

CDW and ACP backgrounds, supporting the analytical findings in figure 2. In all the cases, a single and local defect is first nucleated on the ground-state lattice configuration and further lattice relaxation induces excess spin or charge density in the defect centres. Although the photoexcitations are finalized into $S^0\uparrow - \tilde{S}^{0\downarrow}$ and $S^- - \tilde{S}^+ +$ pairs along paths 1 and 2, respectively,
Figure 5. The same as figure 3 but for the fourth excited state. When \( l = 4 \), \( f_{\mu, s}^{(3)} = 1 \) for \( \mu \leq 3N/2 \) and \( f_{\mu, s}^{(0)} = 0 \) for \( \mu > 3N/2 \) but \( f_{3N/2-1, \uparrow}^{(3)} = 0 \) and \( f_{3N/2 + 2, \uparrow}^{(3)} = 1 \).

Figure 6. The same as figure 5 but with an ACP (\( \sigma = -1 \)) background.

The early kinks on path 2 convey net spins rather than charges and then even wear charges and spins alternately. This is strong evidence for tunnelling between the energy surfaces \( E_1 \) and \( E_0 \) in figure 2. Kinks seem to be more frequently stabilized into spin solitons than into charged ones at low temperatures (see figure 7 later on). The oscillation between neutral and charged kinks is generally observed on the occasion of their geminate recombinations.

The CDW and ACP backgrounds oscillate at regular intervals but with different frequencies. The CDW oscillation is mainly caused by the halogen sublattice, while the ACP oscillation is by the platinum sublattice. The ratio of the former frequency to the latter one is indeed \( \sqrt{2M_M/M_X} \approx 2.4 \). Figures 3(3) and 4(3) demonstrate in common that a newborn soliton–antisoliton pair survives twice the oscillational period.
and then recombines to disappear. ACP solitons are consequently longer-lived than CDW solitons.

Next we pump up an electron to the fourth excited state. Typical examples are shown in figures 5 and 6. Now far distant defects in a pair, accompanied by excess spin and charge densities all along, suddenly appear within much less than picoseconds, which is again consistent with the analytical findings in figure 2. Any defect is more delocalized on an ACP background than on a CDW background and polarons find them in the centres of them. Such striking fluctuations of spin and/or charge densities alternate, but even their signs are oscillating, in the centres of them. Such striking fluctuations of spin and/or charge densities are characteristic of photoproducts decaying nonradiatively rather than by luminescence.

5. Summary and discussion

Coexistent neutral and charged solitons as stable photoproducts are characteristic of PtX chains. Mononuclear platinum complexes should be described with larger Coulomb interactions, where neutral solitons are probable photoproducts, while charged solitons are much less expected due to an energy barrier on the way from an STE to them in a pair, as is shown in figure 8. Conversion of photoinduced charge-transfer excitons into neutral soliton pairs has been indeed detected in the chloro and bromo complexes, [Pt(en)2Cl](ClO4)2 and [Pt(en)2Br](ClO4)2 [39, 53–55]. The photoinduced valence anomalies are all ESR-active and a comparative study of the heterometal compound [Pt(en)2][Pd(en)2Br2](ClO4)2, whose ground state is no longer degenerate, enables us to distinguish spin solitons from polarons.

No doubt the simultaneous stabilization of neutral and charged solitons against STEs is attributable to the reduction of Coulomb interactions, but they owe much to the binuclear unit-assembled structure as well. When we artificially model PtX chains with a similar set of correlation and coupling parameters as adopted in the present PtX chains, charged solitons indeed look available from STEs, but neutral solitons turn hardly reachable instead, as is shown in figure 9. Such a situation more or less agrees with experimental findings in Pt–I chains. There is a report [42, 43] that photocarriers in [Pt(en)2I](ClO4)2 may be charged solitons. Since the halogen

![Figure 7. Characterization of photoproducts at the moment of four picoseconds after pumping up an electron to the first (a) and fourth (b) excited states with CDW and ACP backgrounds.](image)

**Table 1. Classification of photoproducts.**

| Character       | Configuration | Label |
|-----------------|---------------|-------|
| Neutral soliton | $S^{0+} - S^{-} - S^{-}$ | 1     |
| Charged soliton | $S^{+} - S^{-} - S^{+}$ | 2     |
| Kink with fractional spin and charge | $+ - K^{+} - K^{-}$ | 1 + 2 |
| Kink with neither spin nor charge | $K^{+} - K^{-}$ | 1 2 + |
character increases in the platinum wavefunctions in the order Cl < Br < I, the d–p transfers are enhanced and the Coulomb interactions are therefore suppressed effectively in the iodo complexes. The stabilization of charged solitons instead of neutral ones is thus understandable. The generated charged solitons are rather long-lived, possibly tunnelling through a bumpy potential [43].

The room-temperature conductivity of Pd2(dta)4I is about nine orders of magnitude higher than those of typical PtX complexes [21]. Photocarriers must be highly mobile in Pt2X chains. Spin solitons, charged solitons and polarons are likely to come together on such a fascinating stage. The real-time simulation reveals quantum tunnelling between neutral and charged solitons, breathing motion of charged solitons in a pair, and asymmetry between electron and hole polarons, which are all stimulative toward further experiments.

The band filling of the dta family M2(RCS)2I (M = Pt, Ni; R = CnH<sub>2n+1</sub>) [3, 4, 27, 28] might be varied in general because of their neutral chain structure. Under doping, bipolarons [5, 6, 56–58], that is, doubly charged bound polarons, also come into our interest. Besides Pt2X chains, ladder-shaped PtX complexes have been recently synthesized. [59, 60] exhibiting ground-state variations [61–63].

We hope our calculations will stimulate extensive optical explorations of new varieties of metal–halide complexes.

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References

[1] Che C-M, Herbstin F H, Schaefer W P, Marsh R E and Gray H B 1983 J. Am. Chem. Soc. 105 4604
[2] Clark R J H, Kurmoo M, Dawes H M and Hursthouse M B 1986 Inorg. Chem. 25 409
[3] Bellitto C, Flamini A, Gastaldi L and Scaramuzza L 1983 Inorg. Chem. 22 444
[4] Bellitto C, Desy G and Fares V 1985 Inorg. Chem. 24 2815
[5] Gammel J T, Saxena A, Batistich I, Bishop A R and Philpott S R 1992 Phys. Rev. B 45 6408
[6] Weber-Milbrodt S W, Gammel J T, Bishop A R and Loh E Y Jr 1992 Phys. Rev. B 45 6435
[7] Yamamoto S 2001 Phys. Rev. B 63 125124
[8] Kuwabara M and Yonemitsu K 2001 J. Mater. Chem. 11 2163
[9] Butler L G, Zietlow M H, Che C-M, Schaefer W P, Srivasth S., Grunthaner P J, Swanson B I, Clark R J H and Gray H B 1988 J. Am. Chem. Soc. 110 1155
[10] Kimura N, Ohki H, Ikeda R and Yamashita M 1994 Chem. Phys. Lett. 220 40
[11] Yamashita M, Miya S, Kawashima T, Manabe T, Sonoyama T, Kitagawa H, Mitani T, Okamoto H and Ikeda R 1999 J. Am. Chem. Soc. 121 2321
[12] Yamamoto S 2000 J. Phys. Soc. Japan 69 13
[13] Swanson B I, Stroud M A, Conradson S D and Zietlow M H 1988 Solid State Commun. 65 1405
[14] Kanner G S, Gammel J T, Love S P, Johnson S R, Scott B and Swanson B I 1994 Phys. Rev. B 50 R18682
[15] Yamamoto S 2001 Phys. Rev. B 64 140102(R)
[16] Yamamoto S 2002 J. Phys. Chem. Solids 63 1489
[17] Matsuoka H, Matsuoka T, Kishida H, Takizawa K, Miyasaka H, Sugihara K, Yamashita M and Okamoto H 2003 Phys. Rev. Lett. 90 046401
[18] Yonemitsu K and Miyashita N 2003 Phys. Rev. B 68 075113
[19] Kitagawa H, Onodera N, Ahn J-S, Mitani T, Toriumi K and Yamashita M 1997 Synth. Met. 86 1931
[20] Calzolari A, Alexandre S S, Zamora F and Felice R D 2008 J. Am. Chem. Soc. 130 5552
[21] Kitagawa H, Onodera N, Sonoyama T, Yamamoto M, Fukawa T, Mitani T, Seto M and Maeda Y 1999 J. Am. Chem. Soc. 121 10068
[22] Yamamoto S 2001 J. Phys. Soc. Japan 70 1198
[23] Ikeuchi S, Saito K, Nakazawa Y, Sato A, Mitsumi M, Toriumi K and Sorai M 2002 Phys. Rev. B 66 115110
[24] Ikeuchi S, Saito K, Nakazawa Y, Mitsumi M, Toriumi K and Sorai M 2004 J. Phys. Chem. B 108 387
[25] Borsich S A, Prassides K, Robert V and Solonenko A O 1998 J. Chem. Phys. 109 4562
[26] Wakabayashi Y, Kobayashi A, Sawa H, Ohsumi H, Ikeda N and Kitagawa H 2006 J. Am. Chem. Soc. 128 6676
[27] Mitsumi M, Murase T, Kishida H, Yoshinari T, Ozawa Y, Toriumi K, Sonoyama T, Kitagawa H and Mitani T 2001 J. Am. Chem. Soc. 123 11179
[28] Mitsumi M, Kitamura K, Morinaga A, Ozawa Y, Kobayashi M, Toriumi K, Iso Y, Kitagawa H and Mitani T 2002 Angew. Chem. Int. Edn 41 2767
[29] Ichinose S 1984 Solid State Commun. 50 137
[30] Onodera Y 1987 J. Phys. Soc. Japan 56 250
