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Negative Differential Resistance in MX- and MMX-Type Iodide-Bridged Platinum Complexes

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Supporting Information

ABSTRACT: Negative differential resistance (NDR) was discovered in MX- and MMX-type iodide-bridged platinum complexes for the first time. The low resistance of the complex observed under the large current cannot be explained only by the Joule heat. The intrinsic charge-ordering states are considered to play an important role in the NDR of these compounds.

Nonlinear conduction in organic conductors has been of interest for a few decades.[1,2] An important milestone in these studies is the fast switching effect of the sample resistance.[1] Since its discovery, the fundamental science and application of nonlinear conduction in organic conductors have been extensively studied.[3] In some cases, charge order plays a key role in achieving nonlinear conduction. For example, the low-energy excitations derived from the domain walls or solitons,[3a] the sliding motion of the charge-density waves (CDWs),[4] and the melting of the charge order[5] have been considered as the origin of nonlinear conduction in organic conductors. Recently, the peculiar thyristor-like current (I)−voltage (V) characteristics and direct current−alternating current converter effect were achieved in some charge-ordered organic conductors,[6] which again promoted the study of nonlinear conduction phenomena in charge-ordered materials.[7]

Quasi-one-dimensional (Q1D) halogen-bridged mononuclear metal complexes (MX-type complexes) and dinuclear metal complexes (MMX-type complexes) are other promising candidates exhibiting nonlinear conduction because they form various electronic states including charge-ordering (CO) states. Very recently, Kishida et al. reported the negative differential resistance (NDR), meaning that the voltage appearing on both ends of the sample decreases with increasing current, in an MX-type nickel complex, $[Ni(chxn)_2Br]Br_2$ (chxn = 1*R*,2*R*-cyclohexanediamine).[8] They demonstrated the current oscillation originating from the NDR by using external resistance and a capacitor with $[Ni(chxn)_2Br]Br_2$. In other words, the NDR is a key to realizing oscillation. This result prompted us to study nonlinear conduction of MX- and MMX-type platinum complexes because they form various CO states, whereas $[Ni(chxn)_2Br]Br_2$ forms only a Ni^{3+} average-valence state[9] at any temperature. Furthermore, these platinum complexes have attractive properties such as photoinduced phase transition[10,11] and vapor adsorption/desorption.[12−15] Therefore, MX- and MMX-type platinum complexes have the potential to be functional materials that can change the conduction properties by external stimuli. Herein, we report for the first time the I−V characteristics and NDR observed in Q1D iodide-bridged platinum complexes.

We studied the I−V characteristics of the following complexes, which have relatively high electrical conductivity at room temperature (σ_{RT} = 0.1−4.4 mS cm^{-1}):[15,16]

(i) An MX-type iodide-bridged platinum complex, $[Pt(chxn)_2I]I_2$ (**1**), which forms a $[\cdots Pt^{2+}\cdots I{-}Pt^{4+}{-}I\cdots]$ CDW state (Figure 1a).[16]

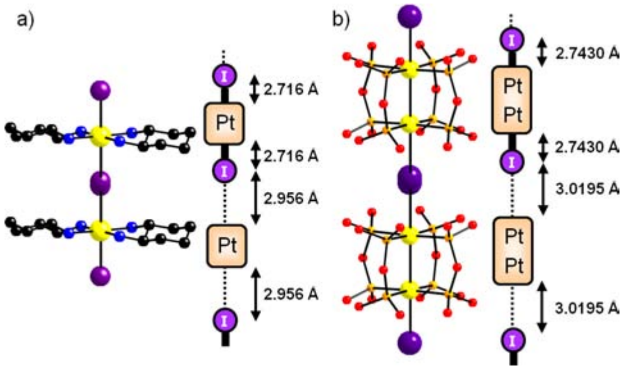

Figure 1. Chain structures of (a) **1** and (b) **2**·$4H_2O$. Color code: black, C; blue, N; red, O; orange, P; purple, I; yellow, Pt. Hydrogen atoms and counterions are omitted for clarity. Bridging iodides are disordered.

(ii) An MMX-type iodide-bridged platinum complex, $K_2A[Pt_2(pop)_4I]\cdot 4H_2O$ (**2**·$4H_2O$; pop = $P_2H_2O_5^{2-}$, A^{2+} = *cis*-$H_3NCH_2CH{=}CHCH_2NH_3^{2+}$; Figure 1b), and $H_3NC_3H_6NH_3^{2+}$ (**3**·$4H_2O$), $H_3NCH_2CHClCH_2NH_3^{2+}$ (**4**·$4H_2O$), and $H_3NC_5H_{10}NH_3^{2+}$ (**5**·$4H_2O$), which form a CDW state $[\cdots Pt^{2+}{-}Pt^{2+}\cdots I{-}Pt^{3+}{-}Pt^{3+}{-}I\cdots]$ in the cases of **2**·$4H_2O$ and **5**·$4H_2O$ and form an alternating charge polarization (ACP)

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+ CDW state $[\cdots Pt^{2+}-Pt^{(2+x)+}\cdots I-Pt^{3+}-Pt^{(3-x)+}-I\cdots]$ in the cases of **3**·4H_2O and **4**·4H_2O.[15,17]

The measurements were carried out in a liquid-helium cryostat. The sample chamber was filled with helium gas (760 Torr at room temperature) during the measurement unless otherwise noted. The *I*−*V* curves were measured by the *I*-driven sweep method.

Figure 2a shows the *I*−*V* curves of **1** at 220, 250, and 300 K. Apparently, the voltage decreased with an increase in the current over 4 × 10^{-5} A at 220 K, which is characteristic of NDR. A similar NDR was observed in **2**·4H_2O below 120 K (Figure 2b) and in its dehydrated complex, **2**, below 140 K (Figure 2c). Because **3**·4H_2O, **4**·4H_2O, **5**·4H_2O, and their dehydrated complexes also showed NDR at low temperature (Figure S1 in the Supporting Information, SI), it can be concluded that NDR is observed as a general phenomenon in MX- and MMX-type iodide-bridged platinum complexes regardless of the CO state of the complexes. These results indicate that the MX- and MMX-type iodide-bridged platinum complexes are good candidates for the current−oscillation devices when they are combined with an external resistor.

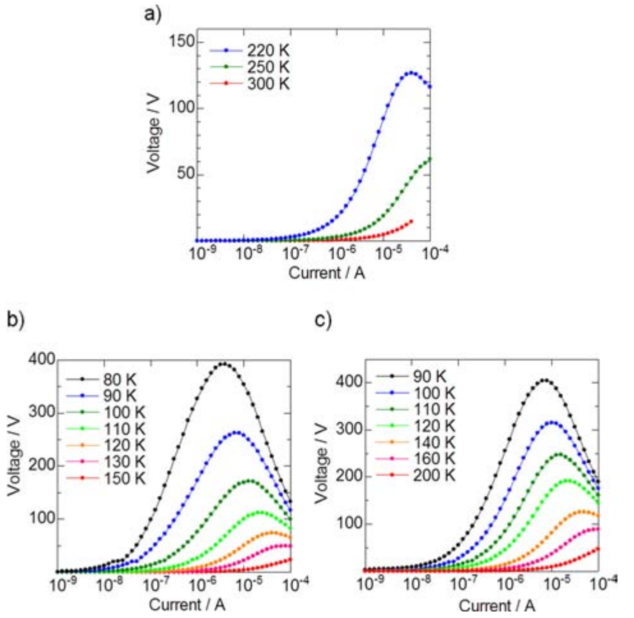

Figure 2. *I*−*V* curves of (a) **1**, (b) **2**·4H_2O, and (c) **2** at various temperatures.

However, it has been known that the NDR effect can also be induced by the Joule heat because the resistivity of the semiconductor decreases as the temperature is increased. Figure 3 shows *I*−*V* curves of **2** at 140 K obtained by the *I*-driven sweep method under two different conditions: the sample chamber was filled with helium gas (filled circles) and the sample chamber was vacuumed continuously (less than 10 Torr) during the measurement (open circles). The black solid line indicates the ohmic *I*−*V* characteristic ($V = RI$), where *R* is the electrical resistance of **2** measured by an applied voltage of 1 V at 140 K. The decrease of the sample resistance from Ohm's law was observed over 10^{-6} A, although the *I*−*V* curves followed it at small current. NDR was observed over 4 × 10^{-5} A in both conditions. Apparently, the applied voltage in the vacuumed condition was smaller than that in the helium-filled condition because the heat efflux from the crystal was prevented and the sample temperature was higher in the former case. Therefore, the Joule heat surely affected the *I*−*V* properties of the present complexes.

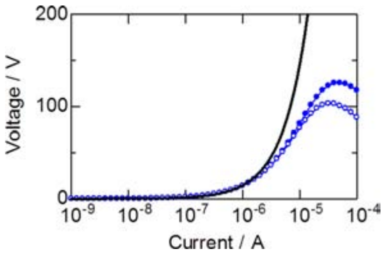

Figure 3. *I*−*V* curves of **2** at 140 K obtained by the *I*-driven sweep method under the conditions that the sample chamber was filled with helium gas (filled circles) and was vacuumed continuously (open circles). The black solid line indicates the ohmic *I*−*V* characteristic at 140 K.

In order to evaluate the effect of the Joule heat, we measured the sample voltage (V_{sample}) of **2**·4H_2O under constant current ($I = 1 \times 10^{-4}$ A) in various pulse widths (Δt). Figure 4 shows the dependence of V_{sample} on Δt at 120 K. It should be noted that V_{sample} reached a constant value when the pulse width was over 50 ms, indicating that the influx and efflux of heat was in equilibrium.

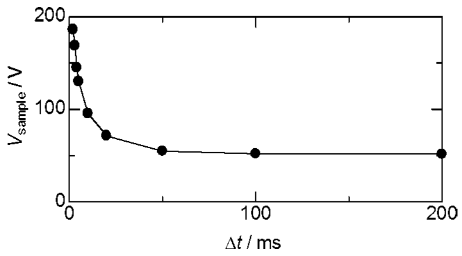

Figure 4. Dependence of V_{sample} of **2**·4H_2O on Δt at 120 K when $I = 1.00 \times 10^{-4}$ A.

On the assumption that the Joule heat is completely converted into a uniform temperature change (ΔT) of the entire sample (adiabatic approximation), ΔT in each Δt was estimated by the procedure described in the SI and is summarized in Table 1 with the values of the resistance. In the case of $\Delta t = 2$ (ms), ΔT was estimated to be 8.9 K; thus, the temperature of the crystal was 128.9 K when V_{sample} was measured (at the end of the pulse). According to the temperature dependence of the electrical resistance of **2**·4H_2O under the low applied voltage (Figure S3 in the SI), the resistance at 128.9 K was 3.7 MΩ (estimated resistance under the Joule heat, R_{heat}). On the other hand, the observed resistance (R_{obs}) was calculated from the applied voltage (186 V) and the current (1 × 10^{-4} A) to be 1.9 MΩ. Because of the adiabatic approximation and neglect of the increase of the molar heat capacity at constant pressure ($C_{p,m}$)

Table 1. Estimated Temperature Change (ΔT) and Resistance under the Joule Heat (R_{heat}), Observed Resistance (R_{obs}), and Ratio R_{obs}/R_{heat} of 2·4H_2O at 120 K When $I = 1.00 \times 10^{-4}$ A

Δt/ms	ΔT/K	R_{heat}/MΩ	R_{obs}/MΩ	R_{obs}/R_{heat}
2	8.9	3.7	1.9	0.51
3	12.9	2.4	1.7	0.71
4	16.5	1.7	1.5	0.88

caused by the Joule heat, ΔT was overestimated, but nevertheless R_{obs} was half of R_{heat}. Therefore, the low resistance observed under large current (1×10^{-4} A) cannot be explained only by the Joule heat. Other factors related to the CO state (CDW state) of **2**·4H_2O should contribute to NDR. Considering the previous studies of the organic conductors,[3−6] the movement of charged solitons (Figure S4 in the SI) and the sliding motion of the CDW are possible origins of nonlinear conduction in **2**·4H_2O. It has been known that a small amount of impurities such as the chain terminals and mobile solitons typically exists in the crystal of MX- and MMX-type complexes.[16,18−20] As shown in Figure S4 in the SI, the charged soliton is estimated to locate at the mismatch of the doubly degenerate CDW phases and to be moved by the applied electric field. In addition, the chain terminals probably pin the CDW phase, which slides at high voltage to reduce the electrical resistance of the crystal.

To the best of our knowledge, this is the first observation of NDR based on the charge-ordered Q1D coordination polymer. The similar *I*−*V* curves in complexes other than **2**·4H_2O in this study suggest that both the Joule heat and CO state contribute to NDR as well as in **2**·4H_2O. The effect of the Joule heat, which depends on the crystal size, obscures the difference in the NDR effect in each CO state (the ACP + CDW state in **3**·4H_2O and **4**·4H_2O and the CDW state in other complexes). However, the similarity of NDR in each CO state suggests that the NDR effect in the ACP + CDW state was probably derived from dominance of the CDW character, which is confirmed by the nonmagnetic properties[15a,20] and optical spectra.[15b] Further analysis and exploration of NDR in MX- and MMX-type complexes are currently going on.

In summary, we observed NDR in MX- and MMX-type iodide-bridged platinum complexes for the first time. Both the Joule heat and CO state of the complexes contribute to the NDR effect. This study opens a new avenue for designing a molecular-based thyristor responsive to vapor irradiation and photo-irradiation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S4 and experimental details for the measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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