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Bromide-bridged palladium(III) chain complexes showing charge bistability near room temperature†

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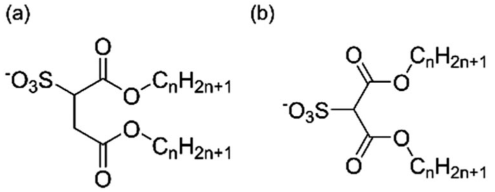
We synthesized and characterized bromide-bridged Pd(III) chain complexes, $[Pd(en)_2Br](MalC_n{-}Y)_2{\cdot}H_2O$ (en = ethylenediamine; $MalC_n$–Y = dialkyl sulfomalonate; *n*: the number of carbon atoms) (*n* = 7 and 12). The compound with *n* = 7 showed charge-bistability near room temperature. In addition, it is shown that the Pd(III) state is maintained in the thin film state.

Bistable molecules, in which two stable states can be switched by external stimuli, such as temperature, light, electric and magnetic fields, and pressure, are promising for a variety of applications, such as memory devices,[1a–d] sensors,[1e–f] actuators,[1g] *etc.* Furthermore, condensed molecular solids showing cooperative bistability can exhibit gigantic stimulus response, although such materials are rare. Quasi-one-dimensional (Quasi-1D) halogen-bridged metal complexes (MX complexes) are aggregated bistable materials, which can show charge bistability, such as the averaged valence (AV) or the Mott-insulating state and the mixed valence (MV) or the charge-density-wave state. MX complexes have 1D electron systems composed of d_{z^2} orbitals of the metal ions (M = Ni, Pd and Pt) and the p_z orbitals of bridging halides (X = Cl, Br and I), forming an MV state, represented as $-M^{IV}-X\cdots M^{II}\cdots X-M^{IV}-$, or an AV state, represented as $-M^{III}-X-M^{III}-X-M^{III}-$. These electronic states are thought to be Peierls–Hubbard systems,[2] in which electron–lattice interactions (*S*), on- and inter-site Coulomb repulsions (*U* and *V*, respectively), and transfer integrals (*T*) compete with each other. In particular, the competition between *S* and *U* is the main factor that determines the electronic state. Thus, all Ni complexes should be in AV states, whereas Pd and Pt complexes should be in MV states due to the *U* values of each M ion ($U_{Ni} \approx 6.0$ eV;[3] $U_{Pd} \approx 1.5$ eV;[4] $U_{Pt} \approx 1.0$ eV, ref. 2). Although MX complexes have the potential for charge bistability, until recently, there were no reports of a material showing both states. However, our research group have recently reported a series of Pd–Br complexes, $[Pd(en)_2Br](SucC_n{-}Y)_2{\cdot}H_2O$ (**Suc-C*n***; en = ethylenediamine; $SucC_n$–Y = dialkyl sulfosuccinate (Scheme 1a); *n*: the number of carbon atoms), that show charge bistability due to the introduction of alkyl chains as their counter-ions.[5] For example, **Suc-C5** undergoes an MV-to-AV phase transition at a critical temperature (T_C) of 206 K.



Scheme 1 Chemical structure of (a) $SucC_n–Y^-$ and (b) $MalC_n–Y^-$.

With MX complexes, it should be possible to optically switch the electronic states *via* charge-transfer (CT) transitions from X to M or from M to a neighboring M. In fact, optical switching, such as MV-to-AV conversion,[6] and AV-to-metal one[7] and gigantic third-order optical susceptibility[8] have been reported for Pd–Br and Ni–Br complexes, respectively. Most recently, we have reported that **Suc-C5** undergoes an excitation-photon-energy-selective conversion from an AV to a metal or an MV state at low temperature.[9] However, for practical applications, the material has to be in an AV state at room temperature (RT). In other words, T_C should be near or greater than RT. In the present study, we designed a new counterion, $MalC_n$–Y (dialkyl sulfomalonate) (Scheme 1b), to control T_C and prepared a new series of Pd–Br complexes $[Pd(en)_2Br](MalC_n{-}Y)_2{\cdot}H_2O$ (**Mal-C*n***). **Mal-C7** was shown to be in an AV state at RT by using X-ray, magnetic, electric and

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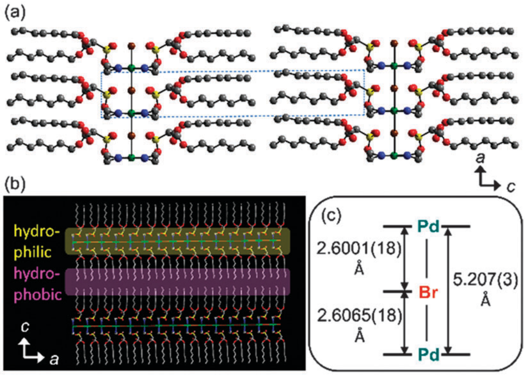

Fig. 1 (a) Crystal structure of **Mal-C7** (293 K). Hydrogen atoms and water molecules are omitted for clarity. Green, Pd; brown, Br; blue, N; yellow, S; red, O; gray, C. Blue dotted lines indicate the unit cell. (b) Crystal packing. (c) Schematic illustration of a 1D chain motif.

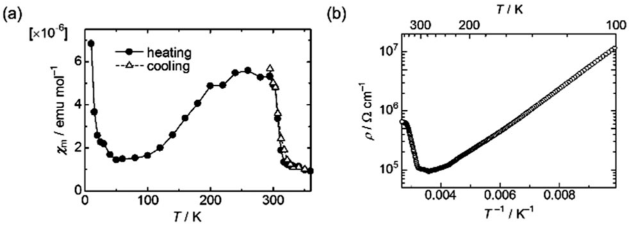

Fig. 2 Temperature dependence of (a) χ_m and (b) ρ for **Mal-C7**.

spectroscopic analyses. In addition, we were able to perform single-crystal X-ray diffraction analysis on **Mal-C7**, resulting in the first crystal structure of a Pd(III) complex in an AV state at RT. Finally, we prepared a thin film for use in an optical device.

A crystal structure of **Mal-C7** at RT is shown in Fig. 1a. **Mal-C7** has a 1D chain structure of infinitely alternating Pd and Br ions. The 1D chain structure is cooperatively maintained by N–H···O hydrogen bonds among the en ligands and oxygen atoms of the sulfonate groups of counterions. In addition, water molecules contribute to hydrogen bonding and support of the 1D chain structure (water molecules are omitted for clarity in Fig. 1). As shown in Fig. 1b, **Mal-C7** has a lamellar structure, in which the hydrophilic 1D space is separated from the hydrophobic space by counterions. These structural features closely resemble those of **Suc-C5**.[5]

In 1D MX chains, the position of bridging halides is strongly related to the electronic state. In other words, if each bridging halide is located at the midpoint between neighboring M ions, the MX complexes are in AV states. In **Mal-C7**, the Pd–Br bond lengths were determined to be 2.6001(18) and 2.6065(18) Å (Fig. 1c), indicating that all bridging Br ions were located at the midpoints of neighboring Pd ions. Furthermore, the neighboring Pd···Pd distance was 5.207(3) Å, which was shorter than 5.26 Å which was the boundary between the MV and AV states reported previously.[5] Thus, **Mal-C7** was structurally expected to be in an AV state at RT. Furthermore, while we could not succeed in determination of the crystal structure at high temperature, the diffuse scattering arising from a disorder or a distortion of bridging X was observed in the X-ray oscillation patterns above 308 K, implying that **Mal-C7** converted from an AV state to an MV state (see ESI†).

In order to confirm that **Mal-C7** was in an AV state at RT, and that it was in an MV state at high temperature, variable-temperature (VT) electron spin resonance (ESR) spectroscopy was performed. Because AV and MV states should display paramagnetic (antiferromagnetic) and diamagnetic behaviors, respectively, the magnetic susceptibilities should be different for both states. VT ESR spectra are shown in ESI.† The temperature dependence of the spin susceptibility (χ_m) obtained by integrating the first derivative of the ESR signal twice is shown in Fig. 2a. Near 310 K, χ_m drastically changed between 5×10^{-6} and 1×10^{-6} esu mol^{-1} at 295 and 330 K, respectively. This result indicated that the electronic state changed from AV to MV states with an increase in temperature with $T_C \approx 310$ K. Furthermore, χ_m gradually decreased with a decrease in temperature below 200 K, which was probably due to a spin-Peierls transition, which has been observed for $[Ni(chxn)_2Br]Br_2$ (chxn = 1*R*,2*R*-diaminocyclohexane)[10] and other materials, such as organic conductors[11] and $CuGeO_3$.[12] This phenomenon is currently being study.

Next, we conducted electrical conductivity measurements. In Fig. 2b, the temperature dependence of the electrical resistivity (ρ) along the *a* axis (1D chain direction) is shown. The ρ value was *ca.* 10 MΩ cm at 100 K, and semiconducting behaviour was observed when temperature was increased. Then ρ started to increase at 310 K, indicating a conversion from AV to MV states. The value of ρ continued to increase steeply until the temperature reached 350 K. Such behavior has also been observed for **Suc-C5**, suggesting a charge fluctuation due to a AV–MV conversion accompanied by CT.[6] Therefore, at RT, **Mal-C7** is in an AV state. Differed from the ESR study, the electrical properties during the heating and cooling processes did not correlate with each other (see ESI†), most likely due to deterioration of the crystal surface at high temperature. Thus, we cannot discuss the differences in ρ during heating and cooling.

Polarized Raman and IR spectra were acquired to obtain further information about the electronic state. In Raman spectroscopy, the $Br–Pd^{IV}–Br$ symmetrical stretching mode ($\nu(Br–Pd^{IV}–Br)$) is allowed in an MV state, whereas it is forbidden in an AV state. A Raman peak at *ca.* 125 cm^{-1} assigned to $\nu(Br–Pd^{IV}–Br)$ gradually appeared above 310 K (see ESI†). In addition, in IR spectroscopy, the vibrational energy of the N–H symmetrical stretching mode (ν(N–H)) of the in-plane ligands depends on the valence of the metal ion to which it is coordinated.[13] In other words, two kinds of ν(N–H) corresponding to Pd^{II} and Pd^{IV} are observed in an MV state, whereas only one ν(N–H) assigned to Pd^{III} is observed in an AV state. For **Mal-C7**, ν(N–H) were observed in the range of 3080–3150 cm^{-1} (see ESI†). Below 310 K, only one peak at 3115 cm^{-1} was observed. And this peak split into two peaks at 3100 and 3130 cm^{-1} above 310 K. In other words, the electronic state changed from an AV to an MV state.

Finally, the temperature dependence of the CT energy (E_{CT}), which was estimated from polarized reflectivity spectra and optical conductivity spectra (see ESI†), is shown in Fig. 3a. E_{CT} for **Mal-C7** was *ca.* 0.6 eV below RT. This value and the temperature dependence are consistent with those for **Suc-C5** in an AV state.[5] In the AV state, the lowest electronic transition was assigned to a CT transition from the lower Hubbard band

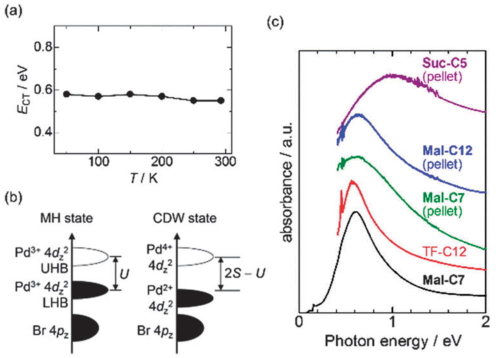

Fig. 3 (a) Temperature dependence of E_{CT} for **Mal-C7**. (b) Schematic illustration of the band structures of Pd–Br AV (left) and MV (right) states. (c) Optical conductivity spectrum of **Mal-C7** (black line) and UV-vis-NIR spectra of TF-C12 (red line) and of KBr pellets of **Mal-C7**, **Mal-C12** and **Suc-C5** (green, blue and purple lines, respectively). All spectra were recorded at RT. A signal at 0.4 eV in TF-C12 is derived from the SiO_2 substrate.

(LHB) to the upper Hubbard band (UHB) (Fig. 3b left). In this state, $E_{CT} \approx U$ if V and T are neglected. Thus, E_{CT} is independent of temperature and Pd···Pd distance. On the other hand, the lowest electronic transition is a CT transition from Pd^{II} to a neighbouring Pd^{IV} sites in an MV state. Here, $E_{CT} \approx 2S - U$ if V and T are neglected (Fig. 3b, right). Since S depends on Pd···Pd distance (and temperature), E_{CT} should be temperature dependent in an MV state. Thus, on the bases of these results, we concluded that **Mal-C7** was in an AV state at RT.

To test the possibility for practical applications, we fabricated a thin film of **Mal-C*n*** and studied its optical absorption properties. Herein, for simplification, we call an aggregate of nanocrystals deposited on a transparent substrate a "thin film". In the case of conventional MX complexes, there are two problems in fabricating thin films: (1) vacuum deposition methods are unavailable, and (2) few MX complexes can be dissolved in organic media while maintaining their 1D chain structures. However, the latter disadvantage can be overcome by introducing alkyl chains in the in-plane ligands or counterions[14] due to the hydrophobic nature of the alkyl chains. We believed that **Mal-C*n*** was suitable for fabricating thin films by using a spin coating process because of its hydrophobic counterions. By elongation of alkyl chains, a thin film of **Mal-C12** (TF-C12) was actually prepared using poly(methyl methacrylate) (PMMA) as a matrix polymer (see ESI†). In Fig. 3c, photon-energy dependence of absorbance for several Pd compounds is shown. Single crystals of **Mal-C7** (black line), TF-C12 (red line) and KBr pellets of **Mal-C7** and **Mal-C12** (green and blue lines, respectively) displayed a peak at 0.6 eV, indicating their electronic states of AV, whereas the KBr pellet of **Suc-C5** (purple line) which was in an MV state displayed a peak at 1.0 eV. Hence, **Mal-C12** is in an AV state even in the thin film state, and thus TF-C12 is promising for optical switching.

In summary, we designed a new counterion and used it to prepare a new 1D bromide-bridged Pd chain complex, **Mal-C7**, which was in an AV state at RT. The electronic ground state was characterized by using both structural and spectroscopic studies. To the best of our knowledge, for the first time, we determined the crystal structure of a Pd(III) chain complex in an AV state at RT. In addition, we prepared a thin film of **Mal-C12** for use in practical applications and are currently studying its optical switching abilities.

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Notes and references

1 (*a*) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; (*b*) J. A. Real, A. B. Gaspar and M. C. Muñoz, *Dalton Trans.*, 2005, 2062; (*c*) T. Akutagawa, H. Koshinaka, D. Sato, S. Takeda, S. Noro, H. Takahashi, R. Kumai, Y. Tokura and T. Nakamura, *Nat. Mater.*, 2009, **8**, 342; (*d*) D. Miyajima, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata and T. Aida, *Science*, 2012, **336**, 209; (*e*) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762; (*f*) A. Bousseksou, G. Molnár, L. Salmon and W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313; (*g*) F. Terao, M. Morimoto and M. Irie, *Angew. Chem., Int. Ed.*, 2012, **51**, 901.

2 (*a*) K. Nasu, *J. Phys. Soc. Jpn.*, 1984, **52**, 3865; (*b*) S. M. Webber-Milbrodt, J. T. Gammel and A. R. Bishop Jr, *Phys. Rev. B*, 1992, **45**, 6435; (*c*) K. Iwano and K. Nasu, *J. Phys. Soc. Jpn.*, 1992, **61**, 1380.

3 H. Okamoto, Y. Shimada, Y. Oka, A. Chainani, T. Takahashi, H. Kitagawa, T. Mitani, K. Toriumi, K. Inoue, T. Manabe and M. Yamashita, *Phys. Rev. B*, 1996, **54**, 8438.

4 (*a*) H. Okamoto, T. Mitani, K. Toriumi and M. Yamashita, *Mater. Sci. Eng., B*, 1992, **13**, L9; (*b*) H. Okamoto and T. Mitani, *Prog. Theor. Phys. Suppl.*, 1993, **113**, 191.

5 (*a*) S. Takaishi, M. Takamura, T. Kajiwara, H. Miyasaka, M. Yamashita, M. Iwata, H. Matsuzaki, H. Okamoto, H. Tanaka, S. Kuroda, H. Nishikawa, H. Oshio, K. Kato and M. Takata, *J. Am. Chem. Soc.*, 2008, **130**, 12080; (*b*) M. Yamashita and S. Takaishi, *Chem. Commun.*, 2010, **46**, 4438.

6 H. Matsuzaki, M. Yamashita and H. Okamoto, *J. Phys. Soc. Jpn.*, 2006, **75**, 123701.

7 (*a*) S. Iwai, M. Ono, A. Maeda, H. Matsuzaki, H. Kishida, H. Okamoto and Y. Tokura, *Phys. Rev. Lett.*, 2003, **91**, 057401; (*b*) S. Iwai and H. Okamoto, *J. Phys. Soc. Jpn.*, 2006, **75**, 011007.

8 (*a*) Y. Iwasa, E. Funatsu, T. Hasegawa, T. Koda and M. Yamashita, *Appl. Phys. Lett.*, 1991, **59**, 2219; (*b*) H. Kishida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi and Y. Tokura, *Nature*, 2000, **405**, 929.

9 H. Matsuzaki, M. Iwata, K. Iwano, S. Takaishi, M. Takamura, M. Yamashita, H. Okamoto, 2014, submitted.

10 S. Takaishi, Y. Tobu, H. Kitagawa, A. Goto, T. Shimizu, T. Okubo, T. Mitani and R. Ikeda, *J. Am. Chem. Soc.*, 2004, **126**, 1614.

11 (*a*) J. W. Bray, H. R. Hart Jr, L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee and J. C. Bonner, *Phys. Rev. Lett.*, 1975, **35**, 744; (*b*) B. van Bodegom, B. C. Larson and H. A. Mook, *Phys. Rev. B*, 1981, **24**, 1520; (*c*) K. Mukai, N. Wada, J. B. Jamali, N. Achiwa, Y. Narumi, K. Kindo, T. Kobayashi and K. Amaya, *Chem. Phys. Lett.*, 1996, **257**, 538.

12 M. Hase, I. Terasaki and K. Uchinokura, *Phys. Rev. Lett.*, 1993, **70**, 3651.

13 K. Okaniwa, H. Okamoto, T. Mitani, K. Toriumi and M. Yamashita, *J. Phys. Soc. Jpn.*, 1991, **60**, 997.

14 (*a*) N. Kimizuka, S. H. Lee and T. Kunitake, *Inorg. Chem.*, 2000, **39**, 389; (*b*) S. Tao, T. Miyagoe, A. Maeda, H. Matsuzaki, H. Ohtsu, M. Hasegawa, S. Takaishi, M. Yamashita and H. Okamoto, *Adv. Mater.*, 2007, **19**, 2707.