Electronic Supplementary Information

for

Bromide-Bridged Palladium(III) Chain Complex Showing Charge Bistability Near Room Temperature

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Experimental details

Single crystal structure was determined on a Bruker APEX II CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). X-ray oscillation photographs were taken on a Rigaku Saturn 724 CCD diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å). ESR spectra were measured on a Bruker EMX spectrometer equipped with a gas-flow type cryostat Oxford ESR 900. The absolute value of the spin susceptibility was evaluated by comparing the first integrated ESR spectrum of the external standard, CuSO$_4$·5H$_2$O. Electrical resistivity measurements were carried out using a Keithley 2601 sourcemeter with a constant voltage of 1.0 V-nanovoltmeter. Two-probe method was employed for the measurement, on which gold wire was attached to the crystal by carbon paste. Polarized Raman spectra were measured on a Renishaw Raman spectrometer. Polarized Fourier transform infrared (FT-IR) spectra were measured on JASCO FT/IR-6200 YMS combined with JASCO infrared microscope ITR-5000 in transmission mode. Polarized reflectivity spectra were obtained by using a specially designed spectrometer with a 25 cm grating monochromator and an optical microscope. All of the measurements above were carried out by using single crystal of Mal-C7. $^1$H nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance 500 500 MHz Nuclear Magnetic Resonance Spectrometer. High-resolution electrospray ionization time-of-flight mass (ESI-TOF-MS) spectra were acquired on Waters Xevo G2 Tof. UV-Vis-NIR spectra were measured on Shimadzu UV-3100 in transmission mode. Thin film was fabricated by using Mikasa 1H-D7 spincoater.

All reagents were purchased from Wako, TCI, Aldrich and Mitsuwa Chemical Co. Ltd. (Japan) and used without further purification.
**Synthesis of sodium salt of diheptyl sulfomalonate Na(MalC\textsubscript{7}Y)**

\[
\begin{array}{c}
\text{HO} & \text{O} & \text{O} & \text{RO} \\
\text{O} & \text{O} & \text{OR} & \text{O} \\
\text{SO} & \text{3} & \text{Na} \\
\end{array}
\]

Na(MalC\textsubscript{7}Y) was synthesized by slight modification of the previous report.\textsuperscript{1} Diheptyl malonate was synthesized from malonic acid and 1-heptanol by the Fischer esterification method with the yield of 76%. Then, obtained diester (6.65 g, 22.1 mmol) was dissolved into dehydrated dichloromethane (20 ml) under N\textsubscript{2} atmosphere. The resulting solution was cooled in ice bath, then added 1.48 ml (2.59 g, 22.2 mmol) of chlorosulfonic acid with stirring. After stirred in ice bath for 30 min, pale yellow solution was refluxed for 2 h under N\textsubscript{2}. Removal of solvent under reduced pressure yielded pale yellow oily liquid. It was dissolved into 50 ml of the mixture of ethanol and water (1/4 (v/v)), added 1.93 g (23.0 mmol) of sodium bicarbonate, and then stirred for 30 min. Resulting solution (pH \approx 7) was evaporated and dry in vacuo, yielding pale yellow solid (7.97 g, 19.8 mmol, 90% based on diheptyl malonate): \textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}\textsubscript{6}) \(\delta\) 0.86 (t, \(J = 6.9\) Hz, 6H), 1.18–1.35 (m, 16H), 1.54 (m, \(J = 6.9\) Hz, 4H), 4.02 (t, \(J = 6.6\) Hz, 4H), 4.39 (s, 1H); ESI-MS (positive) \(m/z\) calcld for C\textsubscript{17}H\textsubscript{31}O\textsubscript{7}SNa\textsuperscript{2+} 425.1586, found 425.1620, (negative) \(m/z\) calcld for C\textsubscript{17}H\textsubscript{31}O\textsubscript{7}S [M−Na]\textsuperscript{−} 379.1790, found 379.1796; Anal Calcd for C\textsubscript{17}H\textsubscript{31}O\textsubscript{7}SNa: C, 50.73; H, 7.76. Found: C, 47.596; H, 7.650.

**Synthesis of sodium salt of didodecyl sulfomalonate Na(MalC\textsubscript{12}Y)**

Na(MalC\textsubscript{12}Y) was synthesized following the synthetic procedure of Na(MalC\textsubscript{7}Y) by using 1-dodecanol instead of 1-heptanol. Yields for didodecyl malonate (white solid) and for sodium salt of didodecyl sulfomalonate (white powder) were 94% based on malonic acid and 92% based on didodecyl malonate, respectively. Analyses for Na(MalC\textsubscript{12}Y): \textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}\textsubscript{6}) \(\delta\) 0.85 (t, \(J = 6.9\) Hz, 6H), 1.15–1.40 (m, 38H), 1.53 (m, \(J = 6.9\) Hz, 4H), 4.005 (t, \(J = 6.5\) Hz, 2H), 4.008 (t, \(J = 6.5\) Hz, 2H), 4.35 (s, 1H); ESI-MS (positive) \(m/z\) calcld for C\textsubscript{27}H\textsubscript{51}O\textsubscript{7}SNa\textsuperscript{2+} 565.3151, found 565.3152, (negative) \(m/z\) calcld for C\textsubscript{27}H\textsubscript{51}O\textsubscript{7}S [M−Na]− 519.3346, found 519.3356; Anal Calcd for C\textsubscript{27}H\textsubscript{51}O\textsubscript{7}SNa: C, 59.75; H, 9.47. Found: C, 54.852; H, 9.478.
**Crystal growth of Mal-C7**

$[\text{Pd(en)}_2]\text{Br}_2$ (6 mg, 15 $\mu$mol) and Na(MalC$_7$–Y) (12 mg, 30 $\mu$mol) were dissolved into methanol/water mixture (3/1 (v/v)). Slow diffusion of Br$_2$ vapor into the solution yielded thin plate-like black crystal of **Mal-C12** within a day: Anal. Calcd for C$_{38}$H$_{80}$BrN$_4$O$_{15}$PdS$_2$: C, 42.12; H, 7.44; N, 5.17. Found: C, 42.019; H, 7.348; N, 5.208.

**Synthesis of Mal-C12**

$[\text{Pd(en)}_2]\text{Br}_2$ (60 mg, 0.16 mmol) and Na(MalC$_{12}$–Y) (160 mg, 0.30 mmol) were suspended into 10 ml of tetrahydrofuran/water mixture (4/1 (v/v)). A drop of Br$_2$ was dropped into the white suspension, yielding black precipitate. The precipitate was collected by suction filter, then washed with large amount of distilled water. After dried in vacuo, 174 mg of black powder was obtained (87% yield based on Na(MalC$_{12}$–Y)): Anal. Calcd for C$_{58}$H$_{120}$BrN$_4$O$_{15}$PdS$_2$: C, 51.07; H, 8.87; N, 4.11. Found: C, 51.129; H, 8.765; N, 4.047.

**Preparation of TF-C12**

3 mg of **Mal-C12** was suspended in 1 ml of chloroform. After an ultrasonic treatment for 5 min, the black suspension was heated up until homogeneous pale yellow solution. The solution was immediately cooled by liq. N$_2$ to be solidified, naturally warmed up to room temperature. The resulting black-green suspension was treated ultrasonication again, then filtered through syringe filter with pore diameter of 1.0 $\mu$m. The filtrate was added 30 mg of PMMA, then sonicated for 5 min and left at rest at room temperature for 3 h. The resulting solution was casted onto SiO$_2$ substrate rotating at 5000 rpm, affording TF-C12.
Table S1. Crystal data and structural refinement parameters for Mal-C7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>Radiation type, Wavelength / Å</td>
<td>Mo Kα, 0.71073</td>
</tr>
<tr>
<td>Formula</td>
<td>C$<em>{38}$H$</em>{80}$BrN$<em>4$O$</em>{15}$Pd$_2$</td>
</tr>
<tr>
<td>Formula mass</td>
<td>1083.49</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
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<td>989698</td>
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<tr>
<td>Crystal size / mm$^3$</td>
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<tr>
<td>a / Å</td>
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</tr>
<tr>
<td>b / Å</td>
<td>8.066(5)</td>
</tr>
<tr>
<td>c / Å</td>
<td>30.666(19)</td>
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<tr>
<td>α / °</td>
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<tr>
<td>β / °</td>
<td>89.103(5)</td>
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<tr>
<td>γ / °</td>
<td>86.149(5)</td>
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<tr>
<td>V / Å$^3$</td>
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</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>T</td>
<td>293(2)</td>
</tr>
<tr>
<td>μ / mm$^{-1}$</td>
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<tr>
<td>ρ$_{calccl}$ / g cm$^{-3}$</td>
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<td>F(000)</td>
<td>569</td>
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<tr>
<td>GOF on $F^2$</td>
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<tr>
<td>$R_1$, wR$_2$ [I&gt;2σ(I)]</td>
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</tr>
<tr>
<td>$R_1$, wR$_2$ [all data]</td>
<td>0.0560, 0.1269</td>
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<tr>
<td>Reflns. measured</td>
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<tr>
<td>θ Range for data collection / °</td>
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<tr>
<td>$R_{int}$</td>
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<td>Flack parameter</td>
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Table S2. Selected bond lengths (Å) and angles (°) for Mal-C7.

<table>
<thead>
<tr>
<th>Selected atoms</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(1)–Br(1) (Å)</td>
<td>2.6001(18)</td>
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<tr>
<td></td>
<td>2.6065(18)</td>
</tr>
<tr>
<td>Pd(1)–N(1) (Å)</td>
<td>2.032(2)</td>
</tr>
<tr>
<td>Pd(1)–N(2) (Å)</td>
<td>2.051(2)</td>
</tr>
<tr>
<td>Pd(1)–N(3) (Å)</td>
<td>2.026(3)</td>
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<td>Pd(1)–N(4) (Å)</td>
<td>2.033(3)</td>
</tr>
<tr>
<td>Br(1)–Pd(1)–Br(1) (°)</td>
<td>179.49(3)</td>
</tr>
<tr>
<td>Br(1)–Pd(1)–N(1) (°)</td>
<td>87.77(6)</td>
</tr>
<tr>
<td></td>
<td>91.84(6)</td>
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<tr>
<td>Br(1)–Pd(1)–N(2) (°)</td>
<td>88.15(6)</td>
</tr>
<tr>
<td></td>
<td>91.56(6)</td>
</tr>
<tr>
<td>Br(1)–Pd(1)–N(3) (°)</td>
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</tr>
<tr>
<td></td>
<td>91.99(8)</td>
</tr>
<tr>
<td>Br(1)–Pd(1)–N(4) (°)</td>
<td>88.03(8)</td>
</tr>
<tr>
<td></td>
<td>92.35(8)</td>
</tr>
<tr>
<td>N(1)–Pd(1)–N(2) (°)</td>
<td>96.29(10)</td>
</tr>
<tr>
<td>N(1)–Pd(1)–N(3) (°)</td>
<td>83.61(11)</td>
</tr>
<tr>
<td>N(1)–Pd(1)–N(4) (°)</td>
<td>179.37(10)</td>
</tr>
<tr>
<td>N(2)–Pd(1)–N(3) (°)</td>
<td>179.83(12)</td>
</tr>
<tr>
<td>N(2)–Pd(1)–N(4) (°)</td>
<td>83.09(11)</td>
</tr>
<tr>
<td>N(3)–Pd(1)–N(4) (°)</td>
<td>97.00(12)</td>
</tr>
</tbody>
</table>
Figure S1. X-ray oscillation photographs of Mal-C7 at various temperature. Red arrows point to the diffuse scatterings.

The photographs were taken in the temperature range 293–323 K. X-ray was irradiated for
120 s at each temperature. Upon increasing temperature, weak diffuse scatterings appeared above 308 K. These scatterings indicate a disorder or a distortion of bridging halides, which is characteristic of an MV state. After cooling to 293 K, the X-ray oscillation pattern completely returned to that before raising temperature.

**Figure S2.** Variable-temperature (VT) ESR spectra for Mal-C7.

![ESR spectrum diagram](image)

**Figure S2.** Variable-temperature (VT) ESR spectra for Mal-C7.

ESR signal for Pd$^{III}$ was observed in the range $2.115 < g < 2.131$ in whole temperature range. The $g$ value got greater and greater upon increasing temperature, indicating the elongation of 1D chain. Another signals which was named impurity were also observed above room temperature. Because, however, those intensities didn’t change upon AV–MV conversion, they were ignored on calculation of $\chi_m$. 
**Figure S3.** Temperature dependence of electrical resistivity for Mal-C7. Measurement was carried out parallel to 1D chain direction (a-axis; \( E||a \)). Solid and broken lines reveal heating and cooling processes, respectively. The heating line is the same data as Figure 3b.

![Temperature dependence of electrical resistivity for Mal-C7](image)

**Figure S4.** Arrhenius plot for Mal-C7. Data were extracted from the heating process. Solid red line is the best fitted line in the range 100–270 K.

![Arrhenius plot for Mal-C7](image)

The raw data were fitted by Arrhenius equation:

\[
\ln(\rho) = \ln(\rho_0) + \frac{E_a}{kT}
\]

where \( \rho_0 \), \( E_a \) and \( k \) represented the electrical resistivity at higher temperature limit, activation energy and Boltzmann constant, respectively. The best fitting in the range 100–270 K (red line in the figure) led us to \( E_a \) of 68 meV. This value is much lower than a half of \( E_{CT} \) (0.58 eV), although we can assume a relation of \( 2E_a = E_{CT} \) for an intrinsic semiconductor. This is probably because of the
existence of a small number of Pd$^{2+}$ ions as impurities, i.e., electron carriers, in an as-grown crystal, which is well-known in most of the MX complexes and has been clarified from the measurement of the DC conductivity and the Seebeck coefficient. Therefore, the conventional MX complexes are not intrinsic semiconductors but n-type ones. This nature leads $E_a$ to be lower than a half of $E_{CT}$.

**Figure S5.** VT polarized Raman spectra for Mal-C7. Polarization is parallel to $a$-axis ($E||a$).

![Raman spectra](image)

**Figure S6.** VT polarized IR spectra for Mal-C7 (left) and the N–H vibrational energy plotted against temperature (right). Polarization is parallel to $b$-axis ($E || b \perp a$). The data in right figure were extracted from the region meshed by blue shadow in left figure.

![IR spectra](image)

IR signs in the energy region higher than 3150 cm$^{-1}$ may be of O–H stretching modes, so that they are neglected.
**Figure S7.** VT polarized reflectivity spectra for Mal-C7. Polarization is parallel to $a$-axis ($E\parallel a$).

Responses near 0.4 eV are assigned to the backside reflections which are sometimes observed in reflectivity spectra for thin films.

**Figure S8.** VT optical conductivity spectra for Mal-C7 ($E\parallel a$).

Optical conductivity spectra were obtained by Kramers–Kronig transformation$^3$ of
polarized reflectivity spectra shown in Figure S7. At each temperature, strong peaks were observed near 0.6 eV accompanied by other responses at lower energy regions. Because the former and the latter are assigned to CT transition and backside reflection, respectively, as mentioned in the footnote to Fig. S7, the latter signals were ignored upon further analyses.

**Figure S9.** Photographs of thin films of (a) TF-C12 and (b) PMMA.

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### References in Supporting Information