Supporting information

An unusual Pd(III) oxidation state in the Pd–Cl chain complex with high thermal stability and electrical conductivity

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Table S1. Crystallographic details of compound **1-Cl**.

	1-Cl
Radiation type, wavelength	Mo Kα, 0.71073 Å
Empirical formula	$C_8H_{24}Cl_3N_4O_4Pd$
Formula weight	453.08 g/mol
Crystal system	Monoclinic
Space group	*C*2
Crystal size	0.58 × 0.04 × 0.03 mm^3
Unit cell dimensions	*a* = 22.3546(18) Å
	b = 4.9468(4) Å
	c = 7.1164(6) Å
	β = 100.900(2)°
Volume	*V* = 772.76(11) $Å^3$
Temperature	100 K
Z	2
Density (calculated)	1.947 Mg/m^3
Absorption coefficient	1.736 mm^{-1}
R_1, wR_2 [$I > 2\sigma(I)$]	0.0333, 0.0558
R_1, wR_2 [all data]	0.0389, 0.0576
F (000)	458
Goodness of fit on F^2	1.017
Absolute structure parameter	0.07(4)

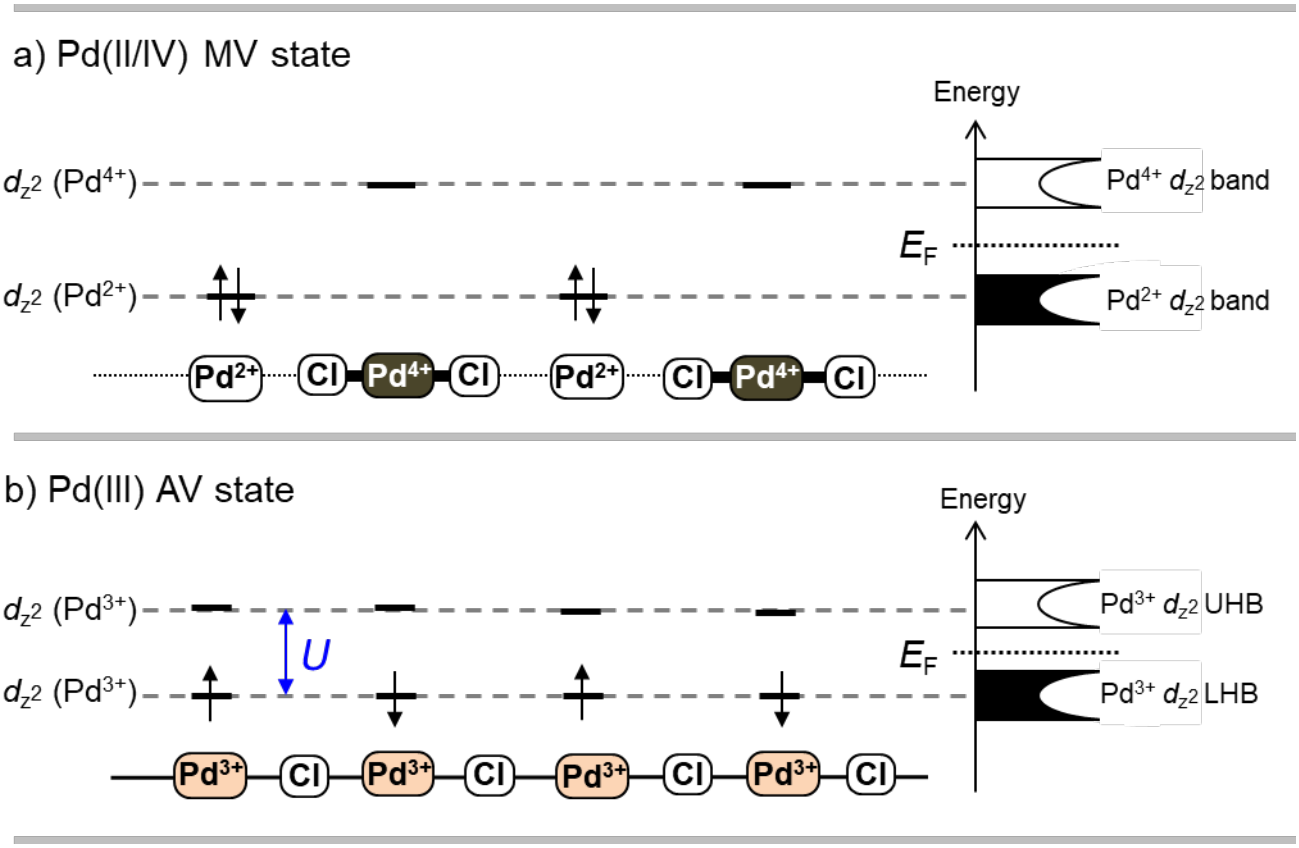

Figure S1. Schematic energy diagram and band structure of a) a Pd(II/IV) MV state and b) a Pd(III) AV state. *U*: on-site Coulomb repulsion, UHB: upper Hubbard band, LHB: lower Hubbard band.

Table S2. Optical gap energy for several PdCl chain complexes

Compounds	Optical gap / eV
$[Pd(NH_3)_2Cl_3]$[S1]	1.65
$[Pd(en)_2Cl](ClO_4)_2$[S2]	2.05
$[Pd(en)_2Cl](BF_4)_2$[S3]	1.86
$[Pd(tn)_2Cl](ClO_4)_2$[S3]	2.03
$[Pd(tn)_2Cl](BF_4)_2$[S3]	1.90
1-Cl	1.0
$[Pd(chxn)_2Cl]Cl_2$[S4]	~1.1
$[Pd(pn)_2Cl](ClO_4)_2$[S3]	2.41
$[Pd(pn)_2Cl](BF_4)_2$[S3]	2.14

en = ethylenediamine, tn = trimethylenediamine, pn = propylenediamine, chxn = 1*R*,2*R*-diaminocyclohexane.

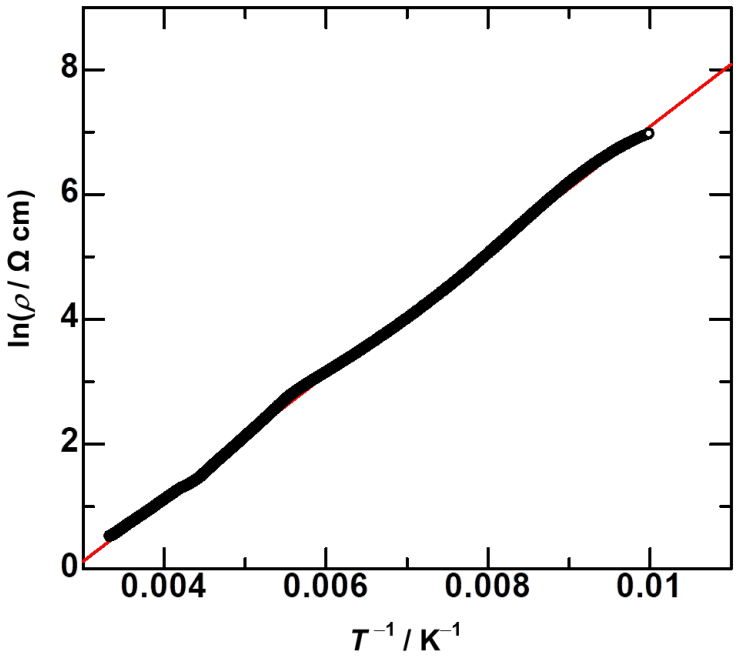

Figure S2. Arrhenius plot for **1-Cl**. Data were extracted from the cooling process. Solid red line is the best fitted line in the range 100–300 K.

The raw data were fitted by Arrhenius equation:

$$ln(\rho) = ln(\rho_0) + E_a/kT$$

where ρ_0, E_a and k represent the electrical resistivity at higher temperature limit, activation energy and Boltzmann constant, respectively. The fitting afforded an E_a value of 86 meV. This value is much lower than half of E_{CT} (1.0 eV), although we can assume the relation $2E_a = E_{CT}$ for an intrinsic semiconductor. This is because of the existence of a small number of Pd(II) ions as impurities, i.e., electron carriers, which has been clarified from the Seebeck coefficient.

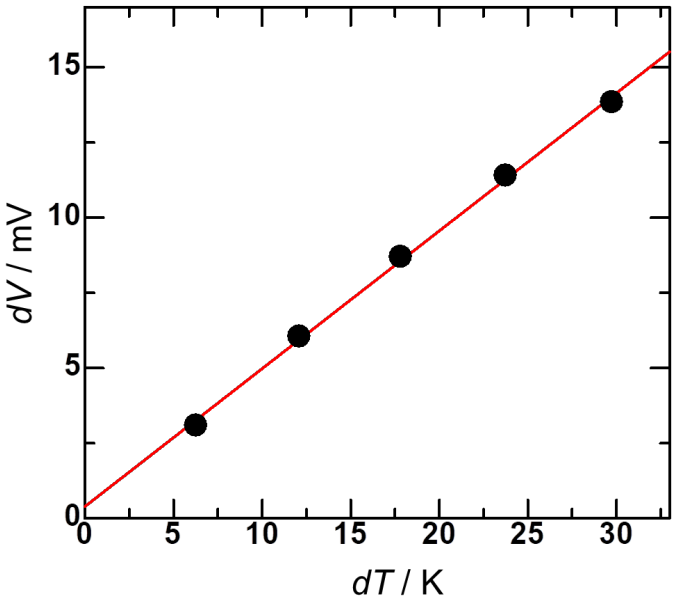

Figure S3. Seebeck coefficient plot for **1-Cl** at room temperature. Solid red line is the best fitted line. Raw data were fitted by equation.

$$dV = -SdT$$

where dV, dT and S represented the voltage difference, temperature difference and Seeback coefficient, respectively. Fitting afforded an S value of –0.458 mV/K.

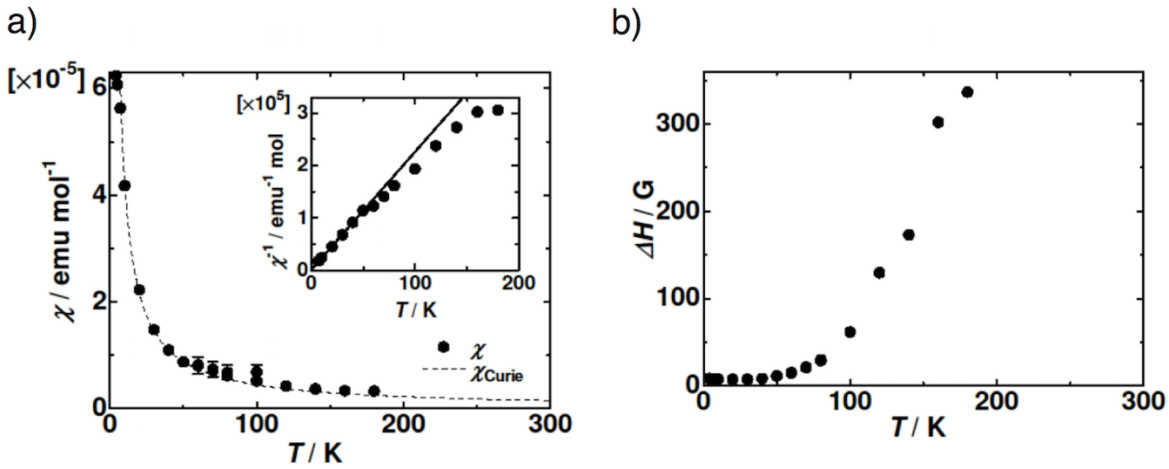

Figure S4. (a) Temperature dependence of the spin susceptibility (χ) of **1-Cl**. The inverse of χ is shown in the inset. (b) Temperature dependence of ESR linewidth (ΔH) of **1-Cl**. ESR signal could not be measured over 200 K due to the extreme broadening.

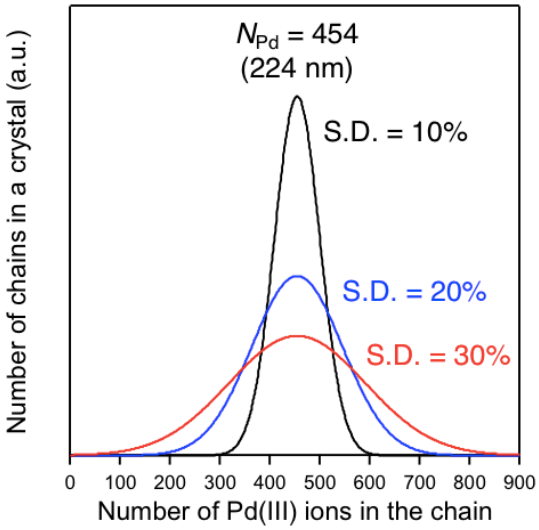

Figure S5. Simulation of the distribution of chain length (number of Pd ions) of **1-Cl** with a standard deviations (S.D.) of 10% (black line), 20% (blue line), and 30% (red line) estimated from the spin impurity level of 0.11% assuming the Gaussian distribution.

References

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