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One-Dimensional Palladium Wires

Michael G. Campbell, David C. Powers, Jean Raynaud, Michael J. Graham, Ping Xie, Eunsung Lee & Tobias Ritter*

One-dimensional metal wires are valuable materials due to their optical and electronic anisotropy, and have potential utility in devices such as photovoltaic cells and molecular sensors¹⁻⁶. However, despite more than a century of research, few examples of well-defined 1-D metal wires exist that allow for rational variation of conductivity. Herein we describe the first examples of one-dimensional Pd molecular wires supported by Pd–Pd bonds, whose thin-film conductive properties can be altered by controlled molecular changes. Molecular wires based on Pd³⁺ give semiconducting films, with bandgaps that correlate to wire length in solution and can be controlled by choice of counteranion. Wires based on Pd^{2.5+} give films that display metallic conductivity above 200 K: a metallic state has not previously been observed for any polymer composed of 1-D metal wires. High-valent palladium complexes featuring metal–metal bonding are uncommon, and all previously reported examples of complexes with Pd–Pd bonds are discrete dipalladium complexes. Due to Pd–Pd bonds, the wires maintain a 1-D polymeric structure in solution and are up to 750 nm long, which corresponds to more than 1000 Pd atoms. Solution stability of the reported Pd wires enables thin film coating, which is requisite for device fabrication using molecular wires³⁻⁵.

One-dimensional chains of metal atoms have long been of interest in both chemistry and physics, and inorganic chemists have studied 1-D coordination complexes with metal–metal interactions since the early 20th century⁷. Most known 1-D metal chains are either mixed-valence oligomers such as the comprehensively studied *platinum*

*blues*⁷⁻¹², or closed-shell 1-D stacks organized by metallophilic interactions that are typically not considered formal metal–metal bonds^{13,14}. There are a few examples of infinite 1-D chains in the solid state with metal–metal bonds, one of the oldest being the family of partially-oxidized tetracyanoplatinates—*Krogmann salts*—formed by bulk oxidation of crystalline samples of Pt(II) complexes¹⁵. More recently, several 1-D rhodium (Rh) chains with metal–metal bonds have been reported, synthesized primarily by electrolytic reduction of Rh(II) complexes¹⁶⁻²⁰. These mixed-valence (d^7 - d^8) Rh wires display infinite 1-D chain structures in the solid state, and exhibit semiconductivity in each case in which the crystal conductive properties have been measured.

Interest in synthesizing 1-D metal chains has been sustained by the unique and useful properties that they display due to their high anisotropy. For example, 1-D wires have found use in applications such as light-emitting diodes, photovoltaic cells, and molecular sensors²⁻⁶. But few examples of 1-D metal chain polymers supported by metal–metal bonds have been reported, which has limited the knowledge of their conductive properties. Even for well-studied oligomeric metal chains, which can be considered as model systems for extended 1-D metal wires, the factors that determine conductivity are a subject of current debate²¹. Unlike conductive organic polymers, for which the principles of controlling conductivity are well established²², examples of polymers based on 1-D metal wires that allow for rational control over conductivity are scarce²³. The development of new 1-D metal chain complexes that offer control over conductive properties is necessary for making progress towards the use of 1-D metal wires in device fabrication. In this report we describe a rapid, high-yielding, scalable, solution-phase synthesis of 1-D Pd molecular wires by self-assembly of dinuclear Pd(II)

complexes upon oxidation. We propose that observed thin film conductivity properties can be controlled by rational modification of the 1-D metal wires.

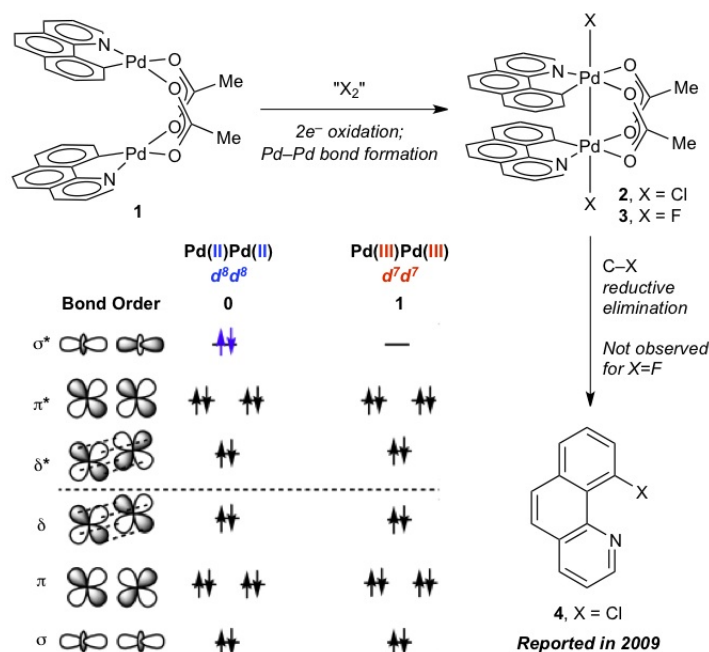


Figure 1 | Synthesis of dipalladium(III) complexes with Pd-Pd bonds. Formation of dipalladium(III) complexes, which can potentially afford C-X bonds via reductive elimination. Complexes 2 and 3 are formed by 2-electron oxidation of dimeric Pd(II) complex 1, which results in a Pd-Pd single bond as rationalized by the qualitative molecular orbital diagram shown (“ X_2 ” is a 2-electron oxidant such as Cl_2 , $PhICl_2$, or XeF_2). C-F reductive elimination from 3 was not observed due to F^- dissociation to give Pd chain complexes (see Fig. 2).

Organopalladium(III) complexes featuring Pd-Pd bonds are uncommon, and have thus far been limited to discrete dipalladium complexes. Since 2009 our lab has investigated the previously unknown role of dipalladium(III) complexes in catalysis²⁴. We have reported the synthesis of dipalladium(III) complexes by oxidation of dipalladium(II) precursors, and their ability to undergo facile carbon-heteroatom reductive elimination (Fig. 1). Our interest in utilizing metal-metal bonding to reduce activation barriers in catalysis led us to investigate carbon-fluorine bond formation from dipalladium(III) fluoride complexes such as 3. Unexpectedly, when targeting 3, we

observed the self-assembly of solution-stable 1-D polymers with a backbone of metal–metal bonds. Treatment of a solution of **1** in CH₂Cl₂ at –50 °C with 1.0 equivalents of XeF₂ led to an immediate color change from pale yellow to dark red (Fig. 2a). Crystallization afforded thermally sensitive, dark red needles of **5**, as infinite chains of cationic Pd(III) nuclei with non-coordinated fluoride anions (Fig. 2b). In the crystal packing of **5**, adjacent polycationic wire strands are collinear, and the voids between the chains are occupied by disordered fluoride counteranions and solvent (Fig. 2c). Due to the high level of disorder in the voids, the fluoride anions were not located in the crystal structure of **5**. Therefore, the presence of fluoride in a 1:1 Pd:F ratio was established chemically by treatment of **5** with TMSCl: both TMSF and Pd(III) dichloride **2** were observed in 97% yield, confirming the assigned molecular formula and the Pd(III) oxidation state in **5**. Crystals of Pd(III) difluoride **3** were isolated alongside crystals of **5**, but redissolved crystals of both **5** and **3** display identical solution spectral features that indicate extended chain structures. Thermal decomposition of solutions of **5** did not provide observable C–F reductive elimination. The data suggests that fluoride coordination to Pd in **5** is reversible, and disfavored in solution.

The acetate-bridged Pd–Pd distance in **5** is 2.72 Å (0.12 Å shorter as compared to **1**), as expected for oxidation of Pd(II) to Pd(III) with concurrent metal–metal bond formation²⁴. The short interdimer Pd–Pd distances (average 2.98 Å) are consistent with unbridged Pd–Pd bonds. Molecular orbital considerations and DFT calculations suggest that the chain structures are supported by Pd–Pd bonds involving symmetry-allowed mixing of 5p_z and 4d_{z²} orbitals on Pd(III), as previously described for attractive metal–metal interactions in Pd(II) and Rh(I) complexes (see Supporting Information, Figures

S1-S4)²⁵. Palladium has not previously been observed to form 1-D complexes with unsupported metal–metal bonds in any oxidation state; additionally, **5** is the first 1-D metal wire with all metal atoms in a d^7 configuration. Molecular wires with an all- d^7 configuration have been postulated to exhibit unique conductive properties¹³, but could not previously be accessed. All previous examples of 1-D chains supported by metal–metal bonding interactions are mixed-valence d^7 - d^8 systems or closed-shell d^8 chains.

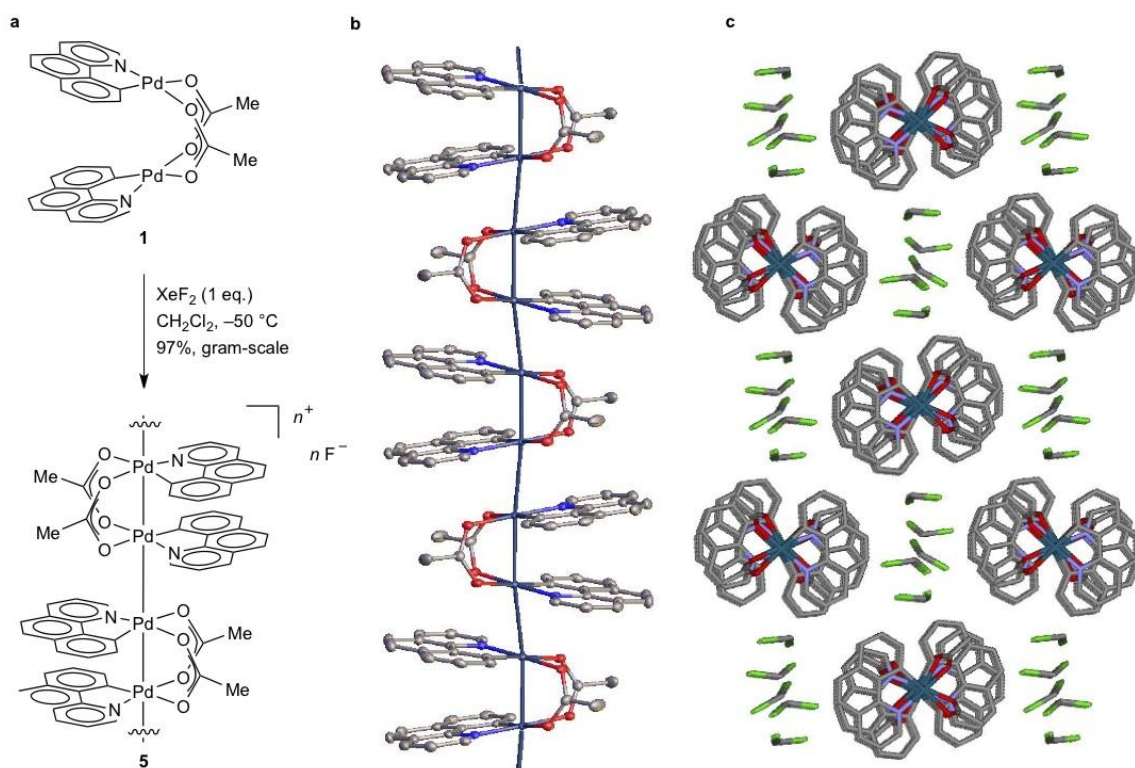


Figure 2 | Synthesis and structure of a 1-D Pd(III) wire. **a**, Synthesis of Pd(III) wire **5**, accomplished in 97% yield on gram-scale by self-assembly of Pd(II) complex **1** upon oxidation with XeF_2 . **b**, X-ray structure of a segment of an infinite chain of **5**, showing unsupported Pd–Pd bonds. **c**, X-ray structure of **5** viewed down the Pd–Pd axis, showing collinear columns of infinite Pd chains, with disordered CH_2Cl_2 in the channels between columns. (Hydrogen atoms and fluoride counteranions not shown in **2b** and **2c**).

Pd(III) wire **5** is soluble in CH_2Cl_2 and spectroscopic methods, including ^1H and ^{19}F nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and ultraviolet-visible/near-infrared (UV-vis/NIR) spectroscopy are consistent with solution-

stable extended chain structures. Static and dynamic light scattering (SLS/DLS) measurements show that **5** exists as an extended rod-like molecule in solution with an average calculated length of 350 nm, corresponding to greater than 600 Pd atoms per wire (Figures S5-S6). UV-vis/NIR absorption spectra of dilute solutions of **5** show a NIR absorption centered around 1000 nm (Fig. 3). The absorption is consistent with solution-stable extended metal chains, in which the metal atoms are in electronic communication through metal–metal bonds^{26,27}. In contrast, discrete Pd(III) dimers such as **2** do not absorb in the NIR region²⁴. The NIR absorption in **5** displays a concentration-dependent red shift that indicates longer chain lengths in solution at higher concentrations²⁶⁻²⁸, which is also supported by the SLS/DLS measurements. In longer chains, optical bandgap decreases, which results in a red shift of the observed absorption. Treatment of dipalladium(II) complex **6** (an analog of complex **1**, with bridging hexanoate ligands instead of bridging acetate ligands to increase solubility) with 1.0 equivalents of XeF₂ followed by 2.0 equivalents of BF₃•OEt₂ gave Pd(III) wire **7**, with weakly-coordinating tetrafluoroborate (BF₄[−]) anions. Solutions of **7** are deep blue in color, and the NIR absorption observed for **7** is red-shifted by 127 nm as compared to **5** at identical concentrations with respect to Pd, indicating increased chain length (Fig. 3). SLS/DLS measurements show an average chain length in solution of 750 nm (400 nm longer than for **5**), corresponding to approximately 1,300 Pd per wire (Figures S7-S8). The longest solution-stable metal chain with assigned length that has previously been reported contains 12 metal atoms¹¹.

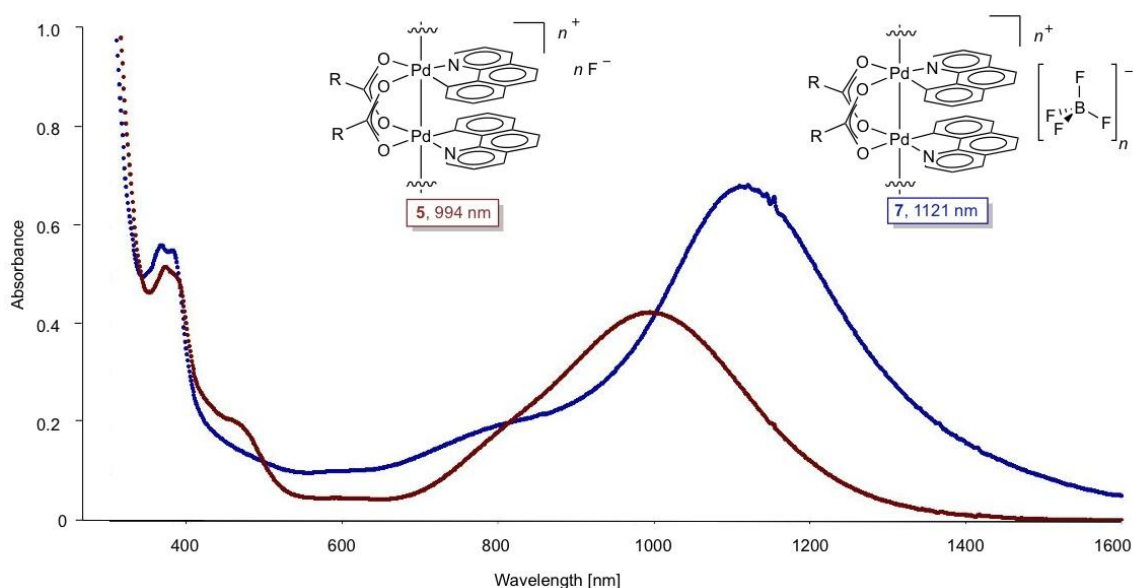


Figure 3 | UV-vis/NIR absorption spectra of Pd(III) wires. UV-vis/NIR absorption spectra of Pd(III) wires **5** and **7** at identical concentrations with respect to Pd, displaying a red shift of 127 nm when fluoride counteranions are replaced by weakly-coordinating BF_4^- anions. (**5**, $\text{R}=\text{Me}$; **7**, $\text{R}=\text{n-C}_5\text{H}_{11}$).

A molecular wire that retains its 1-D polymeric structure in solution can be valuable for the construction of devices with molecular wires^{3,5,22}, but most reported examples of 1-D metal chains supported by metal–metal bonds have been synthesized and studied exclusively in the solid state. To demonstrate the capability for solution processing, we used drop casting to assess conductivity by standard four-point probe measurements. Films deposited from a solution of Pd(III) wire **5** behave as a semiconductor, displaying increasing conductance with increasing temperature in the range of 150–280 K. A bandgap of 1 eV was calculated from linear fitting of $\ln(\text{conductance})$ versus $1/\text{temperature}$ (Figure 4a). By comparison, a film of dipalladium(III) complex **2** behaved as an insulator across the measured temperature range. For Pd(III) wire **7**, with BF_4^- counteranions, thin-film conductivity measurements show a bandgap of 0.7 eV—0.3 eV lower in energy than **5** (Figures S13-S17). The lower electrical bandgap for thin films of **7** as compared to **5** is consistent with the observed red

shift in NIR absorption (Fig. 3). The ability to modify bandgap in semiconducting polymers is valuable for applications such as photovoltaic devices²².

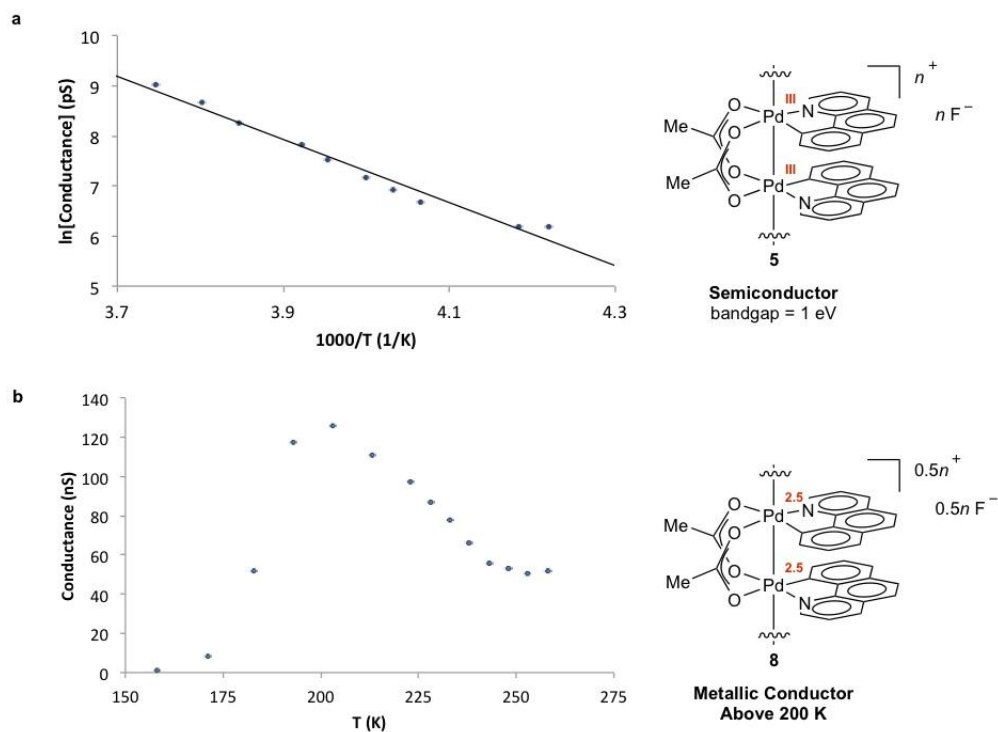


Figure 4 | Temperature-dependent thin-film conductivity of 1-D Pd wires 5 and 8. **a**, Plot of $\ln[\text{conductance}]$ (pS) versus inverse temperature ($1000/K$) for Pd(III) wire **5**, which behaves as a semiconductor. Bandgap is calculated to be 1 eV. **b**, Plot of conductance (nS) versus temperature (K) for Pd(2.5) wire **8**, which displays a metal to insulator transition at 200 K. Data points were obtained from linear fitting of I/V curves at each temperature (Figures S9 and S18).

The change in bandgap from **5** to **7** demonstrates that controlled molecular changes can influence the conductive properties of polymer films of 1-D Pd wires. In addition to adjustment of bandgap through counteranion substitution, modification of electronic properties was effected through variation in Pd oxidation state. Pd(2.5) wire **8** was prepared by treatment of **1** with 0.5 equivalents of XeF_2 under identical conditions used for the preparation of **5**. Only two other complexes containing Pd(2.5) have been reported, both of which exist as discrete dinuclear complexes^{29,30}. Crystals of **8** are dark red needles that can exceed 1 cm in length, and X-ray crystallographic analysis shows an infinite 1-D chain structure analogous to **5**, with one fluoride counteranion per every two

Pd nuclei. At 100 K, the acetate-bridged Pd–Pd distance in **8** is 0.02 Å shorter than in **5**, while the unbridged distances are on average 0.04 Å shorter in **8**. The shorter Pd–Pd distances may be accounted for by a decrease in coulombic repulsion between Pd centers in **8** as compared to **5**²⁹. In contrast to semiconducting films of Pd(III) wire **5** (Fig. 4A), thin-film conductivity measurements of Pd(2.5) wire **8** show that a metal to insulator transition occurs around 200 K (Fig. 4B). A metallic state has not previously been observed for any polymer composed of 1-D metal wires. Because the supramolecular structure within the thin film of **8** is not known, the cause of the metal to insulator transition cannot presently be assigned. One-dimensional conductors are subject to Peierls distortion, in which the conductive electrons are no longer delocalized at low temperature, causing insulating behavior³¹. Variable temperature X-ray analysis of crystals of **8** does not show an apparent structural transition in the range of 100 to 250 K (Figure S22); however, the electronic properties of single crystals and thin films can be different.

Despite decades of interest in the use of 1-D metal molecular wires in devices, to date there has been a lack of synthetic routes to 1-D metal wires that allow for solution processing, or for rational control over conductive properties. Here we have reported the first examples of 1-D Pd wires, which maintain lengths of up to 750 nm in solution due to metal–metal bonds. Thin films cast from solutions of Pd wires display conductive properties that can be controlled by molecular changes: films of Pd(III)-based molecular wires are semiconductors with modifiable bandgap, while films of the Pd(2.5)-based wire display metallic conductivity above 200 K. Future work on connecting molecular structure of the newly accessed Pd wires to the conductivity of single crystals or single

molecules, rather than of polymer films, may provide an advance towards the goal of rationally designing 1-D metal wires.

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Author contributions

M.G.C., D.C.P., J.R. and T.R. conceived and designed the experiments, M.G.C., D.C.P., J.R., M.J.G. and P.X. performed the experiments, M.G.C. and E.L. performed the theoretical calculations and M.G.C., D.C.P., J.R. and T.R. co-wrote the paper.