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One-Dimensional Palladium Wires: Influence of Molecular Changes on Supramolecular Structure

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Supporting Information Placeholder

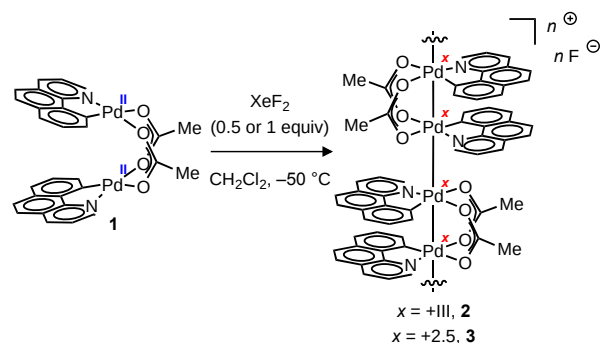
ABSTRACT: Nanostructured materials based on one-dimensional (1-D) metal wires are of potentially utility; however, to date there is a lack of synthetic methods that allow for variation of structure and therefore properties. Here we report the use of molecular control elements to alter the solid-state structures of 1-D Pd wires, including Pd–Pd bond distances and porosity of the supramolecular framework.

One-dimensional (1-D) metal chain compounds, featuring metal–metal interactions, have been studied for more than a century, beginning with the archetypal “platinum blues.”¹ Interest in 1-D metal chains has been sustained by fundamental curiosity about their optical and electrical properties, due to their high anisotropy; in recent years, interest has also grown based on the potential utility of 1-D metal wires in applications such as nanotechnology, molecular sensing, and photovoltaic devices.² A major shortcoming in the field of 1-D metal wire research has been the inability to access wires with systematically varied structures, in order to determine the relationship between structure and properties.

We have reported the synthesis of solution-stable 1-D Pd wires, via self-assembly by Pd–Pd bond formation, upon oxidation of Pd(II) dimers such as **1** (Scheme 1).³ We demonstrated that by controlling the amount of oxidant used, it was possible to access isostructural 1-D Pd wires with average Pd oxidation state of +III (**2**) or +2.5 (**3**). Complexes with Pd in the +III or +2.5 oxidation state are uncommon, and have only recently been studied for their unique structure and reactivity.^{4,5} Oxidation state has an effect on thin-film conductivity: films of Pd(III) wire **2** display semiconductivity, while films of Pd(2.5) wire **3** display a metal to insulator transition at around 200 K. A metallic state had not previously been reported for any polymer composed of 1-D metal wires. These results highlight the possibility of using controlled molecular changes to influence the properties of 1-D metal wires. Here, we report on the effect of molecular changes on the solid-state structure of the 1-D Pd

wires. Controlled changes in Pd oxidation state, counteranion, and supporting ligand scaffold are used to alter Pd–Pd bond lengths as well as porosity of the supramolecular framework. The development of synthetic methods to alter the structures of 1-D metal wires may have an impact on the utility of nanostructured materials based on 1-D wires, and may ultimately allow for synthesis of 1-D wires with rationally tailored properties.

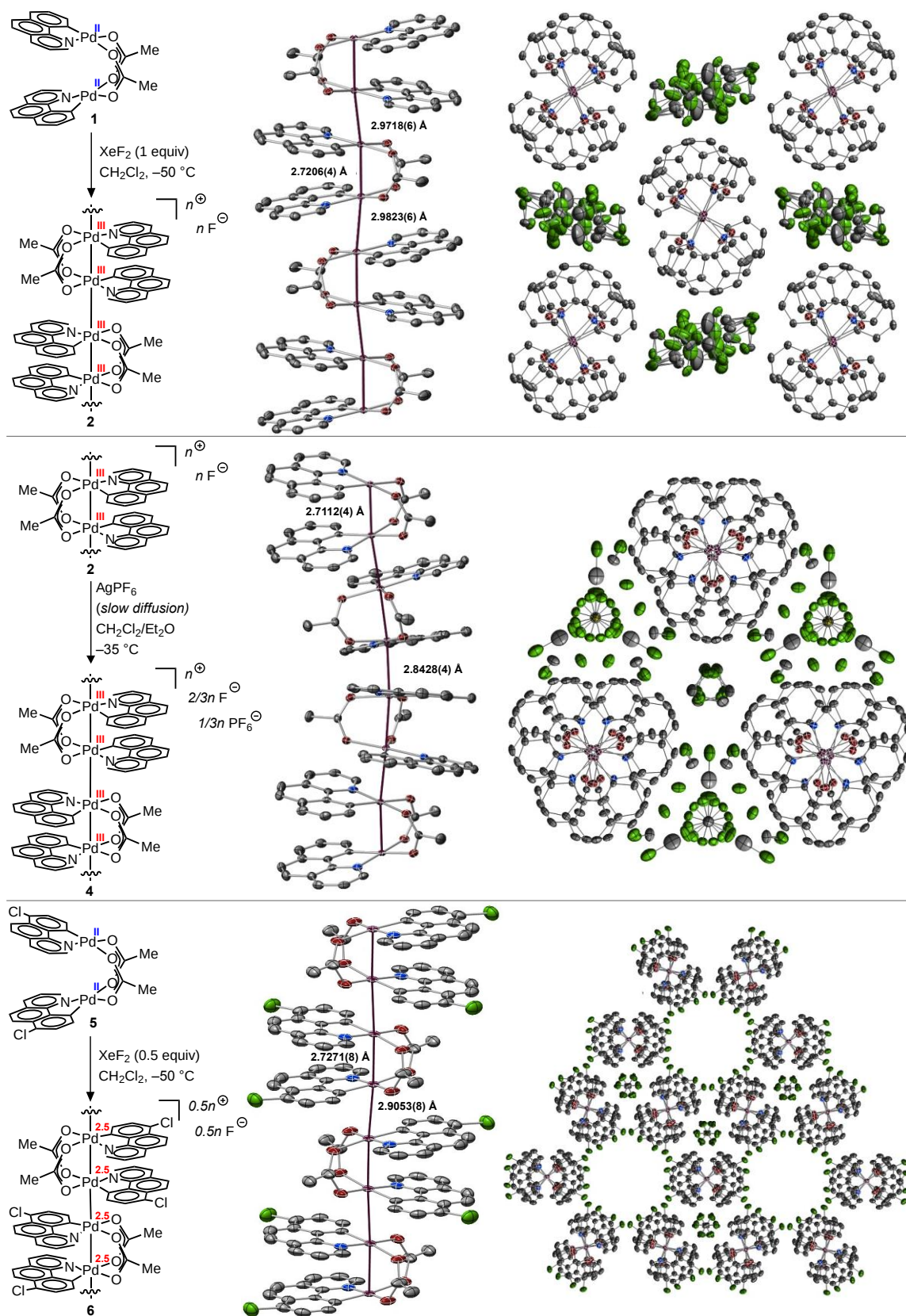
Scheme 1. Self-Assembly of 1-D Pd Wires, with Control of Pd Oxidation State



We were able to take advantage of the solution stability of Pd(III) wire **2** to perform anion metathesis, and examine the effect of counteranion on wire structure. We previously reported that replacement of the fluoride counteranion in Pd(III) wire **2** with more weakly-coordinating anions such as tetrafluoroborate (BF_4^-) resulted in increased average solution-state chain length, from 350 nm to 750 nm, with a concomitant decrease in solubility.³ The counteranion substitution was also shown to have an impact on thin-film conductivity, wherein increased solution-state chain length correlated with a decrease in electrical bandgap; this is consistent with previous reports demonstrating that increased chain length also results in decreased optical bandgap.⁶

Addition of AgPF_6 to a CH_2Cl_2 solution of Pd(III) wire **2** resulted in the immediate precipitation of dark blue solids. Slow diffusion of a Et_2O solution of AgPF_6 into a CH_2Cl_2 solution of **2** at $-35\text{ }^\circ\text{C}$ resulted in the growth of dark blue needle crystals, which were

Scheme 2. Effect of Molecular Changes on Supramolecular Structure of 1-D Pd Wires^a



^a Left: Synthesis of 1-D Pd wires; Middle: Structure of a segment of the 1-D wire, showing Pd-Pd bond distances; Right: Supramolecular architecture viewed down the Pd-Pd bond axis, showing disordered anions and solvent molecules in the pores between the 1-D wires. X-ray structures drawn with 50% probability ellipsoids; H-atoms omitted for clarity.

insoluble in CH₂Cl₂. X-ray crystallographic analysis revealed Pd(III) wire **4**, in which 1/3 of the fluoride counteranions in **2** are replaced with hexafluorophosphate (PF₆[−]) anions (Scheme 2).

The counteranion substitution has a pronounced effect on solid-state structure: while Pd wires **2** and **3** with all fluoride counteranions crystallize in the *P2₁/c* space group, featuring a 2-fold screw axis, Pd(III) wire **4** crystallizes in the *R32* space group, featuring a 3-fold screw axis. The change in crystal packing is accompanied by a significant decrease in the Pd–Pd distance between dimeric units. As shown in Table 1, the interdimer Pd–Pd distance in **4** is 0.1316(4) Å shorter than the average interdimer Pd–Pd distance in **2**. Variations in metal–metal distance can be a key factor in altering the electrical conductivity and optical properties of 1-D metal wires.^{7,8} We were unable to obtain electrical conductivity measurements for the 1-D Pd wire crystals reported in this manuscript due to thermal and atmospheric instability, resulting in decomposition upon attempted electrode attachment.

Table 1. Structural Parameters for 1-D Pd Wires^a

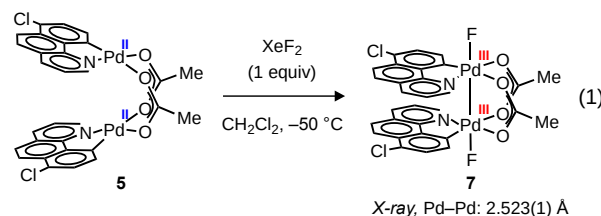
Pd Wire	Acetate-Bridged Pd–Pd Distance	Unbridged Pd–Pd Distance	Pore Diameter
2^b	2.7206(4) Å	2.9718(6) Å 2.9823(6) Å	10.3 Å
3^b	2.7008(4) Å	2.9296(6) Å 2.9531(6) Å	10.2 Å
4	2.7112(4) Å	2.8428(4) Å	10.7 Å, 8.9 Å
6	2.7271(8) Å	2.9053(8) Å	15.2 Å, 9.2 Å

^a Data obtained at 100 K. ^b See reference 3.

In addition to post-synthetic modification of 1-D Pd wires, we also investigated variations in the dimeric Pd(II) building blocks. In general, we found that wire formation is highly sensitive to the nature of the supporting ligand scaffold: the presence of bridging carboxylate ligands with small substituents, such as acetate, seems to be particularly important for wire formation. Substitution of the bridging acetate ligands in **1** with linear aliphatic carboxylates, such as *n*-hexanoate, is tolerated, and can be used as a synthetic handle to increase wire solubility;³ however, Pd(II) dimers featuring sterically more demanding carboxylates, as well as other bridging ligands such as amidates, were not found to give 1-D wires upon oxidation.

Pd(II) dimer **5**, featuring the 7-chlorobenzo[*h*]quinolyl ligand, gave 1-D Pd wire **6**, with average Pd oxidation state +2.5, upon treatment with 0.5 equivalents of XeF₂ in CH₂Cl₂ at −50 °C (Scheme 2). Pd(2.5) wire **6** crystallizes as red needles in the *P3̄c1* space group. X-ray crystallographic analysis is consistent with a 2:1 Pd:F ratio in **6** which, along with spectroscopic data, supports an average +2.5 oxidation state for Pd. As with Pd wires

2 and **3**, in the solid-state structure of **6** adjacent Pd dimers are oriented at 180° with respect to one another. The interdimer Pd–Pd distance in **6** is 2.9053(8) Å, which is slightly shorter than observed for Pd(2.5) wire **3** and Pd(III) wire **2** (Table 1). The similarity in unbridged Pd–Pd distances among the Pd(III) and Pd(2.5) wires may be accounted for by opposing forces of bond order and coulombic repulsion: while the Pd–Pd bond order is higher at the Pd(III) oxidation state, adjacent Pd atoms in Pd(2.5) wires experience weaker electrostatic repulsion due to less buildup of positive charge.^{5b} Attempts to access an isostructural wire with a Pd oxidation state of +III resulted only in the isolation of discrete, fluoride-capped Pd(III) dimer **7** upon crystallization (eq 1). Other attempted modifications of the cyclometallated benzo[*h*]quinolyl ligand of **1** did not result in observable formation of 1-D Pd wires.



A unique feature of the solid-state structure of **6** is the presence of large 1-D pores, organized by the chloride substituent on the cyclometallated ligand (Scheme 2). Crystals of Pd(2.5) wire **6** display two distinct pore sizes, with diameters of 15.2 and 9.2 Å, while Pd(2.5) wire **3** displays a uniform pore diameter of 10.2 Å (Table 1). Remarkably, the 15.2 Å diameter pores of **6** appear to be largely empty in single crystals: the difference map shows only weak, highly delocalized residual electron density peaks inside the 15.2 Å diameter pores, which are not strong enough to support the assignment of solvent molecules or ions. The disordered fluoride anions and CH₂Cl₂ solvent molecules are found to occupy the 9.2 Å diameter pores, stabilized by possible C–H...X hydrogen-bonding interactions, including C_{bhq}–H...Cl, C_{bhq}–H...F and Cl₂HC–H...F (bhq = benzo[*h*]quinolyl ligand). The possibility for such stabilizing interactions is absent in the 15.2 Å diameter pores due to the Cl atoms of the cyclometallated ligand that line the channel. Highly porous nanostructured materials featuring 1-D metal chains are potentially useful for porous electrodes and molecular sensors, and the ability to tune pore size is particularly valuable for such applications.^{2e,9}

Solutions of **6** and **7** display broad near-IR absorbances around 1000 nm that are non-linear with concentration, consistent with the presence of solution-stable 1-D metal chains (Fig 1).³ The spectroscopic data indicates that in CH₂Cl₂ solutions Pd(III) dimer **7** is in equilibrium with 1-D Pd(III) chains; however, fluoride coordination to Pd appears to be favored in the solid state. In contrast to Pd(2.5) wire **6**, solutions of **7** display additional absorbances at 642 and 468 nm, which are also non-linear with concentration. These absorbances are

likely due to the equilibrium with discrete Pd(III) dimer **7**, which is supported by TD-DFT calculations (see Supporting Information); all known Pd(III) dimers display characteristic absorption features in the range of 400–650 nm.^{4b}

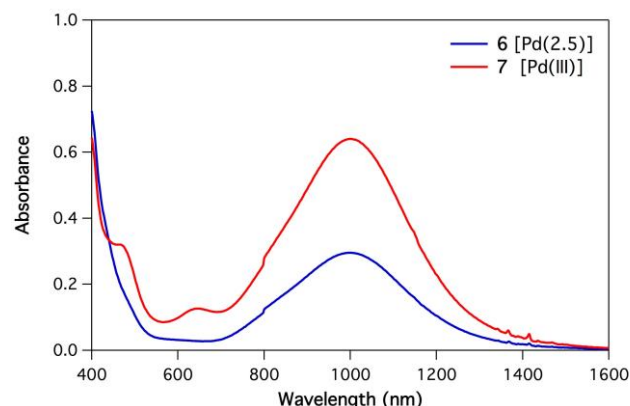


Figure 1. UV-vis/NIR absorbance spectra of **6** and **7** (CH_2Cl_2 , 5 °C, 2.6×10^{-4} M in [Pd]).

In summary, we have investigated the effect of controlled molecular changes on the supramolecular structures of self-assembled 1-D Pd wires. Through variation of Pd oxidation state, ligand scaffold, and counteranion, we have observed changes in Pd–Pd bond distances as well as porosity in crystalline 1-D Pd wires. The ability to control such structural features may have an impact on the technological utility of nanostructured materials based on 1-D metal wires.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and spectroscopic data for all new compounds, details of DFT calculations, crystallographic data for **4**, **6**, and **7** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

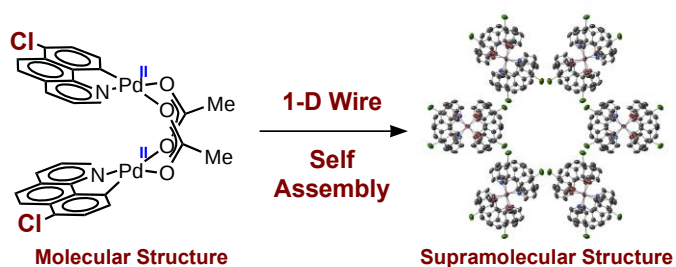
The authors declare no competing financial interests.

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