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

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Supporting Information

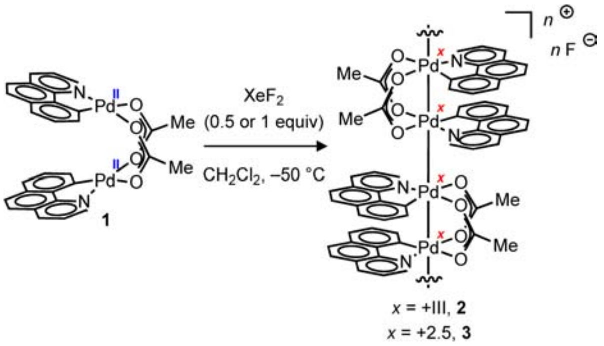
ABSTRACT: Nanostructured materials based on one-dimensional (1D) metal wires are of potential utility; however, to date, there is a lack of synthetic methods that allow for variation of structure and therefore properties. Here we report the use of molecular control elements to alter the solid-state structures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

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

We have reported the synthesis of solution-stable 1D palladium wires, via self-assembly by Pd−Pd bond formation, upon oxidation of Pd(II) dimers such as **1** (Scheme 1).[3] We demonstrated that, through control of the amount of oxidant used, it was possible to access isostructural 1D palladium wires with an 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] These results highlight the possibility of using controlled molecular changes to influence the electronic properties of 1D metal wires. Here, we report on the effect of molecular changes on the solid-state structure of the 1D palladium wires. Controlled changes in the Pd oxidation state, counteranion, and supporting ligand scaffold are used to alter the Pd−Pd bond lengths as well as porosity of the supramoelcular framework. The development of synthetic methods to alter the structures of 1D metal wires may have an impact on the utility of nanostructured materials based on 1D wires, and may ultimately allow for the synthesis of 1D wires with rationally tailored properties.

We were able to take advantage of the solution stability of Pd(III) wire **2** to perform anion metathesis and examine the effect of the counteranion on the wire structure. We previously reported that replacement of the fluoride counteranion in

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



Pd(III) wire **2** with more weakly coordinating anions such as tetrafluoroborate (BF_4^-) resulted in an increased average solution-state chain length, from 350 to 750 nm.[3] Increased solution-state chain length was found to correlate with a decrease in the electrical and optical bandgap, consistent with previous reports.[6] The 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 °C resulted in the growth of dark blue needle crystals, which were insoluble in CH_2Cl_2. X-ray crystallographic analysis revealed Pd(III) wire **4**, in which one-third of the fluoride counteranions in **2** are replaced with hexafluorophosphate (PF_6^-) anions (Scheme 2).

Counteranion substitution has a pronounced effect on the solid-state structure: while palladium wires **2** and **3** with all-fluoride counteranions crystallize in the space group $P2_1/c$, featuring a 2-fold screw axis, Pd(III) wire **4** crystallizes in the space group *R*32, 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 1D metal wires.[7,8] We were unable to obtain electrical conductivity measurements for the 1D palladium wire crystals reported in this manuscript because of thermal and atmospheric instability, resulting in decomposition upon attempted electrode attachment.

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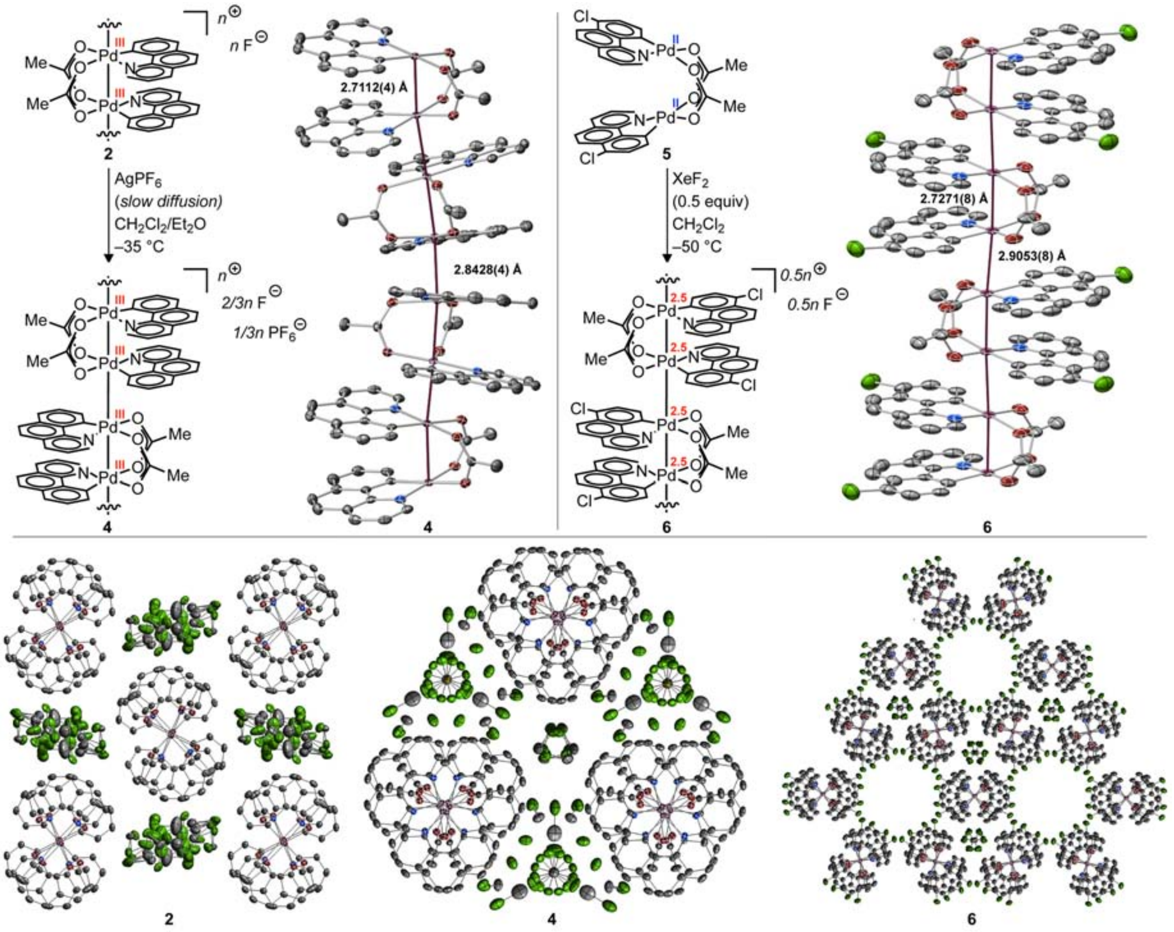
Scheme 2. Effect of Molecular Changes on the Supramolecular Structure of 1D Palladium Wires[a]



[a]Top: Synthesis and X-ray structure of 1D palladium wires **4** and **6**, showing Pd−Pd bond distances. Bottom: Supramolecular architectures viewed down the Pd−Pd bond axes, showing disordered anions and solvent molecules in the pores between the 1D wires. X-ray structures are drawn with 50% probability ellipsoids; H atoms are omitted for clarity.

Table 1. Structural Parameters for 1D Palladium Wires[a]

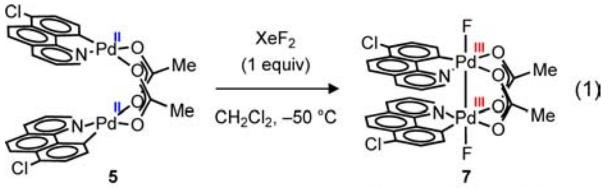
palladium wire	acetate-bridged Pd−Pd distance (Å)	unbridged Pd−Pd distance (Å)	pore diameter (Å)
2[b]	2.7206(4)	2.9718(6) 2.9823(6)	10.3
3[b]	2.7008(4)	2.9296(6) 2.9531(6)	10.2
4	2.7112(4)	2.8428(4)	10.7, 8.9
6	2.7271(8)	2.9053(8)	15.2, 9.2

[a]Data obtained at 100 K. [b]See ref 3.

In addition to postsynthetic modification of 1D palladium 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 were not found to give 1D wires upon oxidation.

Pd(II) dimer **5**, featuring the 7-chlorobenzo[*h*]quinolyl ligand, gave 1D palladium wire **6**, with an average Pd oxidation state of 2.5+, upon treatment with 0.5 equiv of XeF$_2$ in CH$_2$Cl$_2$ at −50 °C (Scheme 2). Pd(2.5) wire **6** crystallizes as red needles in the space group $P\bar{3}c1$. 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 palladium wires **2** and **3**, in the solid-state structure of **6**, adjacent palladium 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 that 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: adjacent Pd atoms in Pd(2.5) wires experience weaker electrostatic repulsion than in Pd(III) wires because of 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 cyclometalated benzo[*h*]quinolyl ligand of **1** did not result in the observable formation of 1D palladium wires.

A unique feature of the solid-state structure of **6** is the presence of large 1D pores, organized by the chloride substituent on the cyclometalated 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



X-ray, Pd–Pd: 2.523(1) 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 CH_2Cl_2 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 Cl_2HC−H···F (bhq = benzo[*h*]quinolyl ligand). The possibility for such stabilizing interactions is absent in the 15.2-Å-diameter pores because of the Cl atoms of the cyclometalated ligand that line the channel. Highly porous nanostructured materials featuring 1D metal chains are potentially useful for porous electrodes and molecular sensors, and the ability to tune the pore size is of particular value.[2e,9]

Solutions of **6** and **7** display broad near-IR absorbances around 1000 nm that are nonlinear with concentration, consistent with the presence of solution-stable 1D metal chains (Figure 1).[3] The spectroscopic data indicate that in CH_2Cl_2 solutions Pd(III) dimer **7** is in equilibrium with 1D Pd(III) chains; however, fluoride coordination to palladium 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 nonlinear 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]

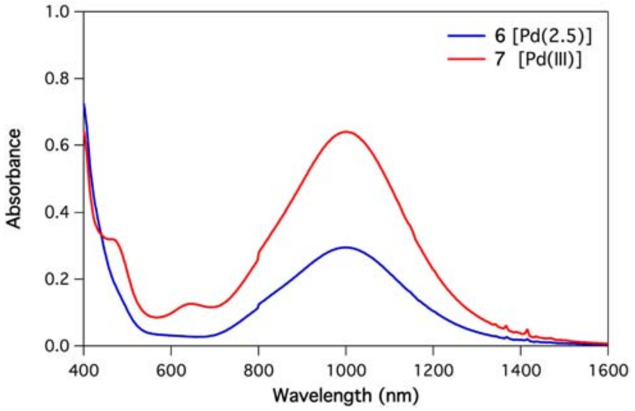


Figure 1. UV−vis/near-IR absorbance spectra of **6** and **7** (CH_2Cl_2, 5 °C, 2.6×10^{-4} M in [Pd]).

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

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and spectroscopic data for all new compounds, details of DFT calculations, and crystallographic data for **4**, **6**, and **7** in CIF format. 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 interest.

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