Metal Atom Wires

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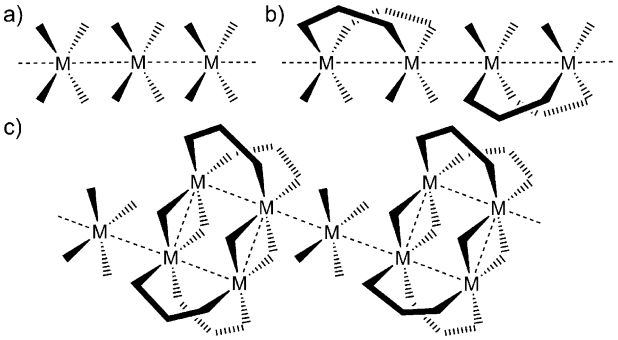
A Motif for Infinite Metal Atom Wires**

*Xi Yin, Steven A. Warren, Yung-Tin Pan, Kai-Chieh Tsao, Danielle L. Gray, Jeffery Bertke, and Hong Yang**

Abstract: *A new motif for infinite metal atom wires with tunable compositions and properties is developed based on the connection between metal paddlewheel and square planar complex moieties. Two infinite Pd chain compounds, $[Pd_4(CO)_4(OAc)_4Pd(acac)_2]$ **1** and $[Pd_4(CO)_4(TFA)_4Pd(acac)_2]$ **2**, and an infinite Pd–Pt heterometallic chain compound, $[Pd_4(CO)_4(OAc)_4Pt(acac)_2]$ **3**, are identified by single-crystal X-ray diffraction analysis. In these new structures, the paddlewheel moiety is a Pd four-membered ring coordinated by bridging carboxylic ligands and μ_2 carbonyl ligands. The planar moiety is either $Pd(acac)_2$ or $Pt(acac)_2$ (acac = acetylacetonate). These moieties are connected by metallophilic interactions. The results showed that these one-dimensional metal wire compounds have photoluminescent properties that are tunable by changing ligands and metal ions. **3** can also serve as a single source precursor for making Pd_4Pt bimetallic nanostructures with precise control of metal composition.*

One-dimensional infinite metal–metal-bond compounds,[1] also known as metal atom wires, or metal atom chain complexes, have attracted much attention for their potential electronic,[2] magnetic,[3] and photoluminescent[4] applications. So far, the majority of such compounds reported are entirely composed of the linear chain motif, which has been demonstrated in the infinite one-dimensional (1D) metal chain compounds of Au,[4b,c] Pt,[5] Pd,[2a,3a,6] Ru,[7] Rh,[2b,c,8] and other heterometallic chain complexes,[2d,4a,9] with few exceptions.[10] As shown in Scheme 1, two types of commonly known linear chain motifs are square-planar (Scheme 1 a) and paddlewheel (Scheme 1 b) metal complexes.[11] For the former, the coordinated ligands need to form a coplanar configuration; thus small ligands, such as NH_3, and large ligands, such as acetylacetonate (acac) and maleonitriledithiolate (mnt), are suitable. For the paddlewheel molecules, bridging ligands, such as acetate (OAc), amide and biimidazole, are necessary components.[12] When they are connected together, the above moieties align in either a nearly straight or a zigzag line. However, other types of motif for infinite metal chain structures are still very rare.



Scheme 1. Motifs for infinite metal chain compounds. Linear type motif composed of a) square-planar and b) paddlewheel molecules. c) New motif described herein.

Herein, we demonstrate a new motif (Scheme 1 c) for metal atom wires using both square-planar and four-membered paddlewheel units. Unlike the previously reported linear chains, this new motif is composed of both a paddlewheel ring and a coplanar configured complex, and the direction of the infinite chain is at an angle with respect to the longest M–M linear unit. We demonstrate that, using this new motif, both homometallic (Pd–Pd) and heterometallic (Pd–Pt) atom wires can be generated by controlling the types of ligands used. This structural flexibility makes it possible to design 1D infinite metal-metal bond compounds with tunable electronic band gaps.

The three types of metal atom chain complexes described herein are $[Pd_4(CO)_4(OAc)_4Pd(acac)_2]$ **1**, $[Pd_4(CO)_4(TFA)_4Pd(acac)_2]$ **2**, and $[Pd_4(CO)_4(OAc)_4Pt(acac)_2]$ **3**. We grew **1** from saturated $[Pd(acac)_2]$ solution in acetic acid (HOAc) under carbon monoxide (CO) atmosphere at room temperature. Complex **2** was generated by adding trifluoroacetic acid (HTFA) into the HOAc/$[Pd(acac)_2]$/CO system. This method of reacting metal acetylacetonate salt with CO and acetic acid can also be applied to prepare a Pd–Pt heterometallic chain complex **3**, following a similar procedure using both $[Pd(acac)_2]$ and $[Pt(acac)_2]$. Scheme 2 shows the synthetic route for **1**, and the experimental details are described in the Supporting Information.

[*] X. Yin, S. A. Warren, Y.-T. Pan, K.-C. Tsao, Prof.Dr. H. Yang
University of Illinois at Urbana-Champaign
Department of Chemical and Biomolecular Engineering
114 Roger Adams Lab, Boc C-3, MC-712
600 S. Mathews Avenue, Urbana, IL 61801 (USA)
E-mail: hy66@illinois.edu
Dr. D. L. Gray, Dr. J. Bertke
University of Illinois at Urbana-Champaign
George L. Clark X-Ray Facility
505 South Mathews Avenue, Urbana, IL 61801 (USA)

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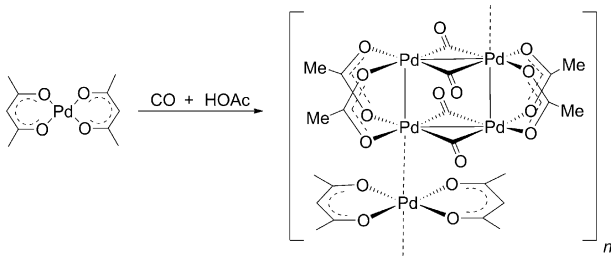
Supporting information for this article, including experimental details, is available on the WWW under http://dx.doi.org/10.1002/anie.201408461.



Scheme 2. Synthetic route for making the 1D metal atom wire compound of **1**.

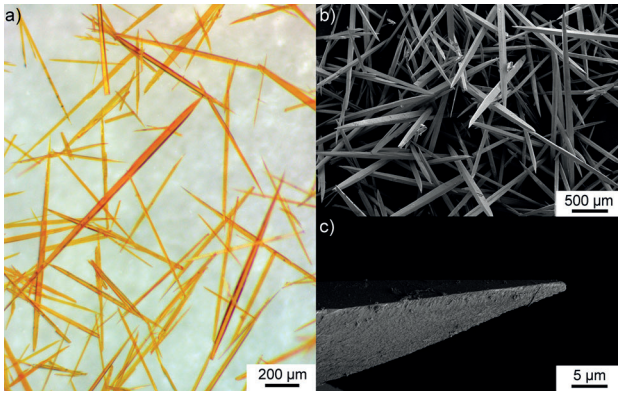


Figure 1. a) Optical micrograph of pristine orange-colored crystals, and SEM micrographs of b) a bundle and c) high magnification of a tip of **1**.

Figure 1 shows the optical micrograph and scanning electron microscope (SEM) images of crystal **1**. Crystal **1** has an orange color and needle-like morphology with approximate dimensions of $4\,mm \times 0.1\,mm \times 0.1\,mm$ (Figure 1a). SEM images show the needle-like crystals have a smooth surface with a sharp tip approximately 1 μm in width (Figure 1b,c). When TFA was introduced to the reaction mixture, square tube-shaped crystals of compound **2** were obtained (Supporting Information, Figure S1). Compound **2** has a reddish color and is stable under ambient atmosphere conditions.

Figure 2 shows the crystal structures of infinite Pd atom chain complexes obtained from single crystal X-ray diffraction (XRD) data. Figure 2a,b shows the perspective and top views of the unit cell for compound **1**, respectively. The unit cell is triclinic with parameters of $a = 9.2625(4)$ Å, $b = 9.7478(4)$ Å, $c = 10.6604(4)$ Å, $\alpha = 94.430(2)°$, $\beta = 112.986(1)°$, $\gamma = 114.727(1)°$. Figure 2c shows the building blocks of **1**. It contains a Pd four-membered ring moiety and a $[Pd(acac)_2]$ moiety. Table 1 summarizes the metal–metal distances in these 1D metal atom chain structures. The Pd four-membered ring is close to a square shape, with a carbonyl-bridged Pd2–Pd3 bond of 2.6747(2) Å in the transverse direction (consistent with a Pd^{I}–Pd^{I} bond),[13] and acetate-bridged Pd2–Pd3#2 distance of 2.8772(2) Å in the longitudinal direction, consistent with the previously reported Pd^{I} four-membered rings.[13] The Pd1–Pd2 distance between the four-membered ring and $[Pd(acac)_2]$ is 3.0866(2) Å in **1**. This Pd–Pd distance is longer than the typical Pd–Pd covalent bond

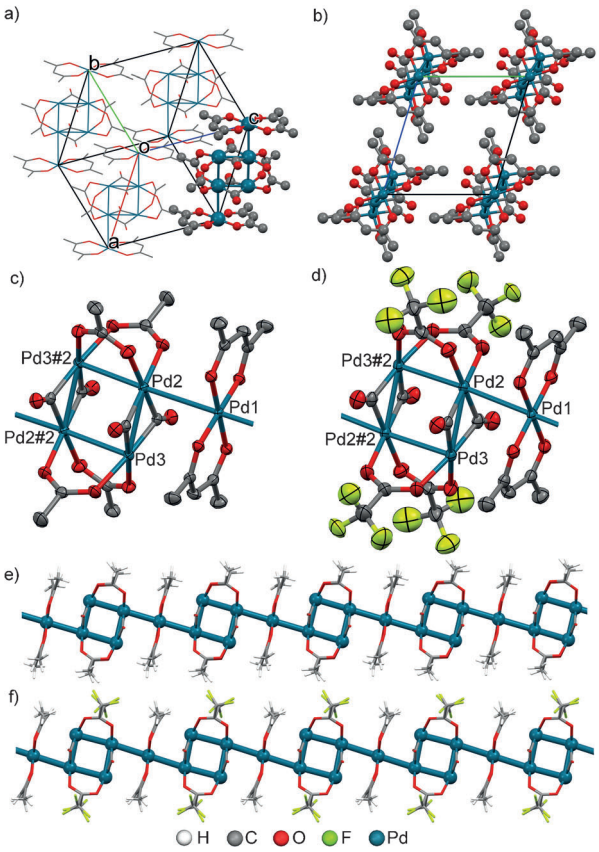


Figure 2. 1D Pd chain structured complexes. a) Unit cell (hydrogen atoms are omitted for clarity), b) view along *a* axis, c) plot of complex **1** (ellipsoids set at 50% probability; H atoms are omitted). d) Plot of complex **2** (ellipsoids set at 50% probability; H and disordered CF_3 atoms are omitted). Infinite 1D Pd chain in e) **1** and f) **2**.[21]

Table 1: Selected metal–metal distances.[a]

Compound	Bond	Length [Å]
1	Pd1–Pd2	3.0866(2)
	Pd2–Pd3, Pd2#2–Pd3#2	2.6747(2)
	Pd2–Pd3#2, Pd2#2–Pd3	2.8772(2)
2	Pd1–Pd2	3.0859(3)
	Pd2–Pd3, Pd2#2–Pd3#2	2.6856(4)
	Pd2–Pd3#2, Pd2#2–Pd3	2.9340(4)
3	Pt1–Pd1	3.0226(5)
	Pd1–Pd2, Pd1#2–Pd2#2	2.6726(5)
	Pd1–Pd2#2, Pd1#2–Pd2	2.8640(6)

[a] Symmetry transformations used to generate equivalent atoms: #2 $-x+1,-y,-z$.

(ca. 2.78 Å),[14] but much shorter than twice the van der Waals radius,[15] shorter than the Pd–Pd distance for metallophilic interactions (3.2 to 3.6 Å),[6b,16] and similar to that reported for the strong Pd–Pd metallophilic interaction.[6c]

Figure 2d shows the analogous units in **2**, replacing the OAc ligand with TFA. The Pd–Pd distances within the Pd_4 ring increased slightly with the change of ligands. The acetate-bridged Pd–Pd distances are Pd2–Pd3#2 = Pd2#2–Pd3 = 2.9340(4) Å and the carbonyl-bridged Pd–Pd bonds are Pd2–Pd3 = Pd2#2–Pd3#2 = 2.6856(4) Å. The unit cell param-

eters of **2** are $a = 9.2137(4)$ Å, $b = 9.5113(5)$ Å, $c = 11.1072(5)$ Å, $\alpha = 87.787(2)°$, $\beta = 70.318(2)°$, $\gamma = 68.077(2)°$.

Figure 2e,f shows the infinite Pd chain structures in **1** and **2**, respectively, with the backbones extended along the *a*-axis. Detailed examination shows that **1** and **2** share the same geometric feature within the infinite chains, that is, the alternatively connected Pd_4 paddlewheel unit and Pd square-planar unit. The Pd1–Pd2 distance between the four-membered ring and $[Pd(acac)_2]$ is 3.0859(3) Å in **2**, which is close to the 3.0866(2) Å Pd1–Pd2 distance in **1**. However, the relative packing positions of infinite Pd chains in **1** and **2** are quite different, which could be due to the different size and electrostatics of methyl and trifluoromethyl groups.

Both Pd and Pt have the same d^8 electron configuration in their β-diketone salts. We further developed an analogous Pd–Pt heterometallic chain compound by introducing $[Pt(acac)_2]$ to co-crystalize with the $Pd_4(CO)_4(OAc)_4$ paddlewheel unit. Figure 3a shows the unit cell of complex **3**, which

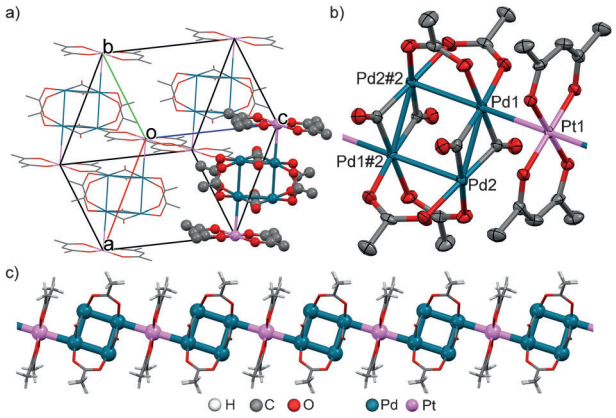


Figure 3. 1D Pd–Pt heterometallic chain structures of **3**: a) unit cell (H atoms are omitted for clarity), b) plot of complex **3** (ellipsoids set at 50% probability; H atoms are omitted), and c) infinite 1D Pd/Pt heterometallic atom chain.[21]

has the same symmetry as that of **1**, with unit cell parameters of $a = 9.282(1)$ Å, $b = 9.704(1)$ Å, $c = 10.629(1)$ Å, $\alpha = 94.190(7)°$, $\beta = 113.250(6)°$, $\gamma = 114.229(7)°$. Figure 3b shows the basic unit in this Pd–Pt bimetallic chain complex **3**. The Pt1–Pd1 distance is 3.0226(5) Å in **3**, shorter than the analogous Pd1–Pd2 distance in **1** and **2**. This Pt–Pd distance agrees with those previously reported,[9d] suggesting a stronger metallophilic interaction between Pt–Pd than between Pd–Pd. The stronger Pt–Pd affinity explains the preferred co-crystallization of $[Pt(acac)_2]$ over $[Pd(acac)_2]$ in this compound. Further inspection of the crystal structure shows that bridging ligands such as CO and OAc/TFA are essential in maintaining the Pd four-membered ring. The acac ligands, which have the coplanar configuration, lie parallel to the carbonyl–Pd plane in the Pd four-membered ring and help maintain the 1D chain structure.

A new synthetic motif can be derived from the above metal chain compounds: a four-membered ring cluster and square-planar molecule are connected alternatively, resulting in a metal atom wire extending in the M_4–M–M_4–M form through metallophilic interactions. The M_4 ring could be stabilized by paddlewheel ligands. The square-planar metal complex could also be modified with various ligands. Thus, a generic structure of infinite atom metal wire becomes feasible for both homometallic and heterometallic atom wire systems.

The photoluminescent (PL) properties of these metal atom chain complexes were examined. Figure 4a shows the

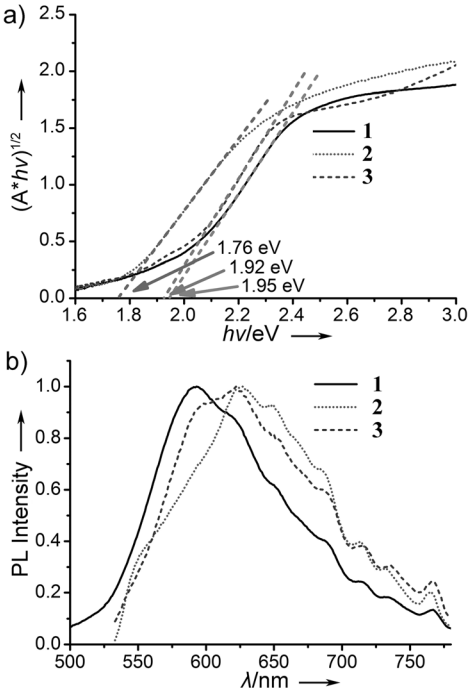


Figure 4. a) Tauc plots based on UV/Vis absorption spectra and b) normalized photoluminescence (PL) spectra of metal chain compounds **1** (592 nm), **2** (625 nm), and **3** (622 nm).

Tauc plots of the solid state UV/Vis absorption spectra of **1**, **2**, and **3** crystals. The following equation was used to analyze the data:[17]

$$(A \times h\nu)^{1/2} = C(h\nu - E_g) \quad (1)$$

where A is the absorbance, h is Planck's constant, ν is the frequency, E_g is the band gap, and C is a proportional constant. The tangent line at the inflection point in the curve is drawn and its intersection point with the x axis is the optical band gap E_g. The optical band gaps of these crystals were measured to be 1.95 eV for **1**, 1.76 eV for **2**, and 1.92 eV for **3**. The cut-off wavelengths in the UV/Vis spectra are approximately 586 nm for **1**, 642 nm for **2**, and 592 nm for **3**. Figure 4b shows the PL spectra of these three compounds. The emission peak is at approximately 592 nm for **1**, 625 nm for **2**, and 620 nm for **3**, though the PL intensity is relatively weak for all these crystals. The photoluminescence lifetime of **3** was determined to be 1.089 ns (Supporting Information, Figure S3).

Band structures of these crystals were calculated using pseudopotential plane-wave code CASTEP[18] with GGA-PBE functional[19] and semi-empirical dispersion interaction corrections.[20] The calculated band structures of 1D metal atom wire compounds **1**, **2**, and **3** are shown in the Supporting Information, Figure S2. The calculated band gaps are 1.893 eV for **1**, 1.729 eV for **2**, and 1.728 eV for **3**, which agree with the experimental values with 2% to 10% error. Density functional theory (DFT) calculations suggest that the band gap could be modified by substituting OAc ligands with TFA ligands in a Pd chain complex with the same motif. The densities of states of these metal atom wire compounds (Supporting Information, Figure S4) show that the substitution of OAc with TFA introduced a shift of valence band to lower energy and incorporation of Pt to the chain motif did not change its band structures significantly. This theoretical result agrees well with the optical band gap analysis.

We found that **1** could serve as a metal precursor in the synthesis of Pd nanoparticles under mild reaction conditions. We also obtained Pd_4Pt alloy by thermal decomposition of **3** in air at 500 °C. The product after the decomposition maintained the original needle shape overall (Supporting Information, Figure S5). A composition of Pd_4Pt was identified by powder XRD (Supporting Information, Figure S6) and energy dispersive X-ray (EDX) analysis (Supporting Information, Figure S7).

In summary, we discovered a new motif for forming infinite homometallic and heterometallic atom wires. Both paddlewheel and square-planar units are necessary in this motif. Carboxylates, amides, or imines could be used as the bridging ligand, and CO could be used as the bridge μ_2 ligand for the paddlewheel subunit, while acac or mnt are optimal for the square-planar subunit. Thus there is good versatility in ligand design. The change of ligands and metal atoms can alter the band gaps, thus affecting the optical and electronic properties of the metal atom wire compounds. This finding creates a new opportunity to study 1D metal atom chain structures and their properties by systematically tuning the ligands and metal backbone, which could benefit the development of new electronic, optical, and magnetic materials.

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[21] CCDC 1016678, 1016680, and 1016681 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

