Conductance and Stochastic Switching of Ligand-Supported Linear Chains of Metal Atoms**

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Molecular wires and switches are forecast to be the elemental building blocks for future electronic applications. Synthesizing 1D molecules and comprehensively understanding their electric characteristics has become one of the major focus areas of materials science. The growth of this research field has been encouraged by the discovery of a strong dependence of electron transport on the length, conjugation, conformation, and substituents of tailored molecules.[1,2] While remarkable progress has been achieved during the past decade, most of the knowledge learned has been from conjugated organic molecules whose counterpart, organometallic molecular wires,[3–17] has been rarely explored.

Herein we present quantitative measurements of single-molecule conductance of 1D multinuclear metal strings ([M\textsubscript{m}L\textsubscript{4}(NCS)\textsubscript{2}], M\textsubscript{m} = Cr\textsubscript{3}, Co\textsubscript{3}, Ni\textsubscript{3}, Cr\textsubscript{5}, Co\textsubscript{5}, Ni\textsubscript{5}, and Cr\textsubscript{7}; L = oligo-\textalpha-pyridylamine; Scheme 1).[3] The conductance values correlate well with the d-orbital electronic coupling between adjoining metal atoms. Among the strings, pentaocta- and heptachromium complexes exhibit stochastic switching events. Such multinuclear strings are important in setting up a perfect platform for the study of metal–metal interactions beyond dinuclear complexes.[18] Complexes up to nonanickel (i.e., M = Ni, m = 3 in Scheme 1, but with Cl axial ligands) have been characterized crystallographically[3] and the length of the ligand extended up to 12 repetitive pyridylamine units (m = 11). While purification and crystallization become increasingly challenging owing to poorer solubility for longer oligomers, preliminary MALDI-MS spectra show that a string of 17 nickel ions (m = 7 in Scheme 1) is obtainable. An understanding of the conduction propagating along the metal chains will further advance progress towards molecular wires for nanodevices.

Figure 1 shows the results of STM (scanning tunneling microscopy) break junction for the trinuclear and pentanuclear string complexes. [20,21] Experimental procedures were documented in detail by the groups of Tao and Lindsay.[20,21]
Briefly housed in a nitrogen-filled chamber, a gold STM tip is brought into and out of contact with a gold substrate in toluene, which also contains the metal strings. Upon repeated formation of the tip–substrate gap, the isothiocyanate axial ligands at the termini of the metal strings bind to the gold. The STM tip is pulled away from the substrate, which results in the formation of the tip–substrate gap, the isothiocyanate axial ligands at the termini of the metal strings bind to the gold, and isolated within an alkane-thiol matrix. The films are then incubated for 1–3 h in dichloromethane containing exp(−βx), in which x is either the number of repetitive units or the molecular dimensions and I is the current. β represents the electronic-coupling strength of the molecule along the electron pathway. A small β value indicates a less significant impedance in electron transport through the molecule. By taking the natural logarithm of the reciprocal of resistance values against the molecular length, we obtain a small tunneling decay constant, 0.50 per Cr atom or approximately 0.21 CC5AE, discernible by STM break junction. The on/off states of the chromium cores are 0, 0.5, and 1.5, respectively; these values indicate the degree of electron delocalization and thus the efficiency of electrons conducting through the metal centers. The resistance of single molecules is also described by a tunneling decay constant, β, approximately given by \( I \times \exp(-\beta x) \), in which x is either the number of repetitive units or the molecular dimensions and I is the current. β represents the electronic-coupling strength of the molecule along the electron pathway. A small β value indicates a less significant impedance in electron transport through the molecule. By taking the natural logarithm of the reciprocal of resistance values against the molecular length, we obtain a small tunneling decay constant, 0.50 per Cr atom or approximately 0.21 Å⁻¹ (see Supporting Information), which makes the Cr strings among the most conductive molecular wires reported.

In addition to their extraordinary conductive properties, the metal strings of penta- and heptachromium complexes show an electric switching phenomenon that is not readily discernible by STM break junction. The on/off states of the two chromium strings are revealed by the conductive atomic force microscopy (CAFM) developed by Lindsay and co-workers. The metal strings are attached to a gold surface and isolated within an n-alkane-thiol matrix. The films are then incubated for 1–3 h in dichloromethane containing

**Figure 1.** a)–f) Single-molecule conductance of metal strings measured by STM break junction. Top panels: typical current curves acquired by stretching the molecular junctions are presented with arbitrary x-axis offsets. Currents and conductance of the metal string complexes decrease in quantized steps. Bottom panels: the conductance histograms are obtained from more than 2000 measurements. The resistance of a single heptachromium string is 6.9 MΩ (see Supporting Information). In the absence of molecules, no such steps or peaks are observed within the same conductance range.
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triarylphosphine-stabilized gold clusters (nominally 2 nm in diameter).\cite{31,32} A metal–molecule–nanocluster junction is configured through the isothiocyanate axial ligands. The gold clusters improve the electrical contact with the gold-coated cantilever of the CAFM and enable highly reproducible current-versus-potential (I–V) measurements for single molecules.\cite{31,32} Figure 2a demonstrates that more than 2500 I–V measurements of the trichromium complex can be grouped into three curves, which converge into one after the values of the curves are divided by $n$ (Figure 2b; $n = 2$ and 3, for the red and blue curves, respectively). Figure 2c is a histogram of the currents measured at a bias of 0.25 V. The strong correlation of an integral multiplicity between the three groups suggests that the one centered at 95 nA corresponds to the primary case of a single trichromium metal string sandwiched between a gold nanocluster and the substrate.

The I–V curves and histograms for all the metal strings show a similar quantized behavior, which is consistent with the findings revealed by STM break junction, although this CAFM approach is complicated by Coulomb blockade.\cite{32} The fundamental curves of the single trinuclear and pentanuclear strings are summarized in Figures 3a and b. Note that the pentachromium string shows two fundamental curves with current values of about 410 and 66 nA at a bias of 1.0 V (blue curves in Figure 3b). The pentachromium string complex also has two sets of I–V curves with 252 and 56 nA at a bias of 1.0 V (see Supporting Information).

readily discernible from their histograms at a bias of 0.25 V are two sets of fundamental current values centered at 74 and 17 nA (Figure 3c) for the pentachromium string, and at 50 and 10 nA (Figure 3d) for the heptachromium string. The dataset of the more conductive complex has a $\beta$ value of 0.16 per Cr atom, thus indicating a stronger electronic coupling than the $\beta$ value of 0.29 per Cr atom derived from the smaller-current dataset to that of the less conductive complex. Although the $\beta$ values are not quantitative owing to Coulomb blockade,\cite{32} the substantial difference between the two values suggests that the two sets of conductance peaks are not due to the S–Au contacts at atop and hollow sites.\cite{31} The ratio of the occurrence of the smaller-current dataset to that of the larger-current dataset is 345:1251 and 970:200 for pentanuclear and heptanuclear complexes, respectively. Tri-, penta-, and heptanuclear complexes were isolated in matrices of n-octanethiol, n-tetradecanethiol, and n-octadecanethiol monolayers, respectively.

The imaging frames of conducting-current mode in Figure 4 show the current toggling between a low value of 17 nA and a high value of about 75 nA. In Figures 4b and c, the current switches between twice that of the less-conductive mode and twice that of the more conductive mode, which suggests the presence of two pentachromium strings underneath the gold nanocluster (Figure 4d). Stochastic on/off switching has been observed in π-electron conjugated systems and alkanethiols. Recent findings narrow down the switching mechanisms to conformation effects\cite{33} on through-
The crystal structures of trichromium strings are sensitive to subtle factors such as solvent and temperature during crystallization, and to different axial ligands. Density functional theory (DFT) calculations of a trichromium analogue, [Cr,(dpa),Cl], by Rohmer and Benard gave a symmetric (i.e., delocalized) structure at the shallow ground state and a conformation with alternating bond lengths at slightly higher states. The calculated energies relative to the symmetric conformation are 0.87 kcal mol$^{-1}$ and 4.25 kcal mol$^{-1}$ for a slightly unsymmetrical (ΔE$_{Cr-Cr}$ = 0.106 Å) and a localized state (ΔE$_{C1-C0}$ = 0.679 Å), respectively. Thus, it is possible that penta- and heptachromium strings with delocalized and alternating Cr–Cr bonds are present simultaneously and that these delocalized and alternating states are interchangeable in the $n$-alkanethiol matrix (Figures 4e and f). However, as there is an energy difference of less than 5 kcal mol$^{-1}$ between the delocalized and localized states of the trichromium complex, the switching rate observed for the pentachromium string is slow. Theoretical studies and variable-temperature experiments will be carried out to elicit the activation energy and switching mechanism.

We have demonstrated that conductance in metal string complexes correlates well with the metal–metal bond order. Penta- and heptachromium strings each exhibit two sets of primary I–V curves, ascribed to conformations of delocalized and alternating Cr–Cr bond lengths; electrons in the latter are localized, which results in a molecular conductance inferior to that of the delocalized conformation. The molecules are stable under ambient conditions and can offer stringent tests of our understanding of interatomic interactions.

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Figure 4. Electric on/off switching of pentachromium strings within an $n$-tetradecanethiol matrix. a)–c) Sequential images and the plots of conducting current versus time were acquired by CAFM at a bias of 0.25 V. The time interval between each frame (30 × 30 nm) was about 3 min. The corresponding current magnitudes indicate that underneath each gold nanocluster (~2 nm in diameter) there is one molecule for (a) and two molecules for (b) and (c). d) Circuit diagram of the apparatus used to take the CAFM measurements showing two sting molecules under the gold nanocluster. e,f) Structures of the penta-chromium metal string with delocalized (on state) and alternating (off state) Cr–Cr bonds, respectively.
