Communication

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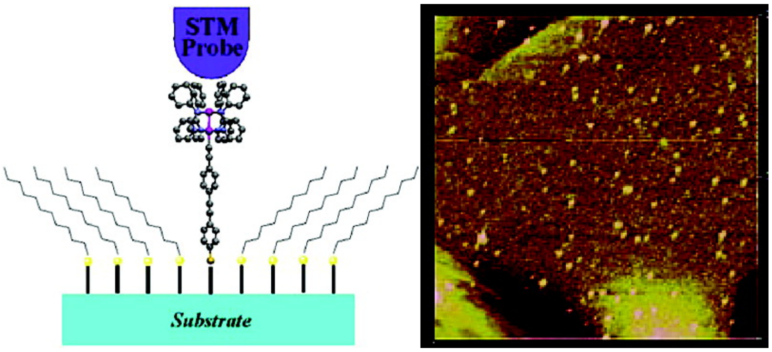
J. Am. Chem. Soc., **2005**, 127 (28), 10010-10011• DOI: 10.1021/ja052604e • Publication Date (Web): 25 June 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

Ru$_2$(ap)$_4$(σ-oligo(phenyleneethynyl)) Molecular Wires: Synthesis and Electronic Characterization

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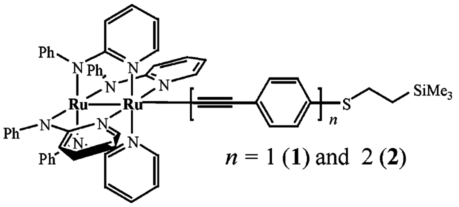
Synthesis of active materials for *molecular electronic devices* has been a focal point of current materials research, with much of the progress based on conjugated *organic* molecules.[1,2] It is noteworthy that the majority of organic molecules utilized so far have HOMO−LUMO gaps (E_g) ranging from 2.4 to 5.0 eV.[2] Clearly, there is still plenty of room for E_g reduction, which should lead to a smaller tunneling decay parameter β and, consequently, higher molecular conductivity.[2] One approach is to incorporate metal complex units into the backbone of conjugated organic molecules, and optimal orbital mixings between metal and organic fragments may result in reduced E_g. Indeed, the series of *trans*-Pt(PR$_3$)$_2$(C≡CC$_6$H$_4$S)$_2$ (R = Cy, Ph, Bu, OEt, and OPh) were shown to be potentially more conductive than OPE (oligophenylene−ethynylene) of comparable lengths through cross-wire junction measurements.[3] Previously, we reported facile electron transfers across the polyyn−diyl chains between two Ru$_2$(ap)$_4$ units (ap = 2-anilinopyridinate) and a remarkably small decay parameter β (0.064 Å^{-1}) from *bulk solution measurements*.[4] Reported in this communication are the synthesis of Ru$_2$(ap)$_4$[σ-(C≡CC$_6$H$_4$)$_n$SCH$_2$CH$_2$SiMe$_3$] (Scheme 1) and the demonstration of molecular wire characteristics.

Synthesis of compounds **1** and **2** was effected by treating Ru$_2$(ap)$_4$Cl with 1 equiv of Li(C≡CC$_6$H$_4$)$_n$SCH$_2$CH$_2$SiMe$_3$, similar to the previous synthesis of Ru$_2$(ap)$_4$(C$_2$R).[5] Cyclic voltammetric (CV) studies of **1** and **2** in THF revealed a reversible 1-e$^-$ oxidation and a reversible 1-e$^-$ reduction (Supporting Information), based on which E_g of compounds **1** and **2** were estimated to be 1.29 and 1.26 eV, respectively. These values are much smaller than the E_g values of the corresponding OPE molecules (3.3−3.5 eV).[2] Compound **1**, shown in Figure 1, has an overall topology very similar to that of Ru$_2$(ap)$_4$(C$_2$Ph)[6] and exhibits bond lengths and angles within the expected ranges. Most significantly, the conjugated backbone defined by the Ru2−Ru1 bond and thiol-capped phenylene−ethynylene is linear. On the basis of the structural data of **1**, the Ru1···S distance in **2** is estimated to be 16.3 Å, which is sufficiently long to warrant insertion into a monolayer of undecanethiol (C11).

Scheme 1. Thiol-Capped Phenyleneethynyl Adducts on Ru$_2$(ap)$_4$ Core



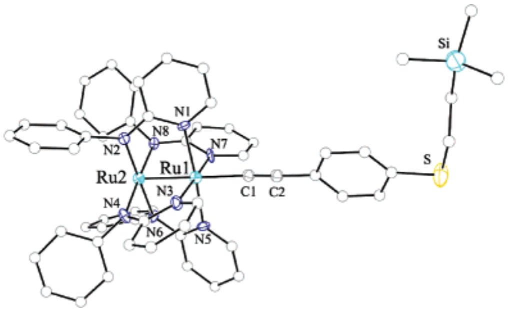


Figure 1. Structural plot of **1**. Selected bond lengths and distances (Å): Ru1−Ru2, 2.3225(3); Ru1−C1, 2.125(3); C1−C2, 1.159(4); Ru1···S, 9.26.

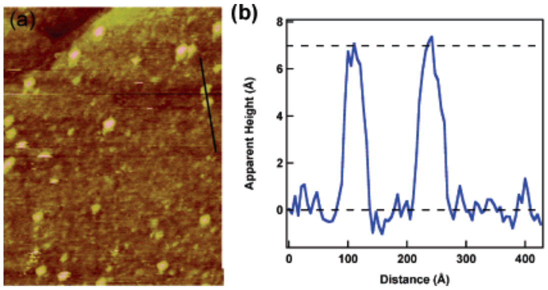


Figure 2. (a) STM image of compound **2** (bright spots) inserted SAM (100 × 75 nm). I_t = 2.5 pA, V_{bias} = 1 V. (b) Black line in (a) indicates cross-section showing apparent height above C11 matrix for two inserted molecules.

CV of compound **2** exchanged into a C11 monolayer on a gold electrode revealed a single redox wave with a formal potential (vs Ag/AgCl) of $E°$ = 0.40 V, which is comparable to the $E_{1/2}$ of 0.43 V measured in THF solution. CV of the C11 SAM on the gold electrode prior to the addition of compound **2** showed no faradic response in the same potential range. In addition, the current increases linearly with increasing scan rate, as expected for surface immobilized species (Supporting Information).[7] Integration of the current−potential waveform of compound **2** in the voltammogram yielded a surface coverage of ca. 5 × 10^{11} molecules/cm^2.

Electronic measurements on compound **2** were carried out on individual molecules or small molecular bundles inserted into a tightly packed self-assembled monolayer (SAM) of C11 (Figure 2a) using scanning tunneling microscopy (STM).[8−12] All STM measurements were performed under ambient conditions in *constant current mode*, at high junction impedance (400 GΩ) such that the tip remains outside the SAM. As has been demonstrated for other molecules inserted into alkanethiol SAMs, **2** displays stochastic switching, which is a random statistical process manifested as molecules that blink on and off in successive STM images.[11−14] Imaging experiments demonstrate that the surface coverage of

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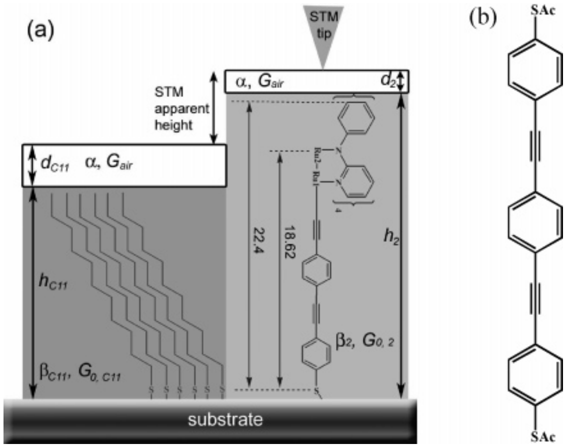

Figure 3. (a) Two-layer STM junction model for compound **2**/C11 SAM. (b) Structure of OPE dithiol.

compound **2** is ~3 × 10^{11} molecules/cm^2, which is in good agreement with CV measurements, especially since stochastic switching can lead to undercounting of the number of molecules due to molecules that stay in the "off" state for the duration of the experiment. From an analysis of 70 insertion events, compound **2** is found to have an apparent height of 7.8 ± 1.1 Å above the C11 matrix (Figure 2b).

While STM images represent a convolution of electronic and topographic information,[15] it is still possible to extract a molecular electronic decay constant β (a measure of the ability to facilitate charge transfer) from images of the molecule inserted into an alkanethiol monolayer. A simple two-layer tunnel junction model, first developed by Weiss et al. for alkane thiols[15] and later demonstrated useful for investigating the charge transport properties of several conjugated molecules by Bjørnholm et al.,[16] relates a molecular β value to the apparent height ($\Delta\text{STM} = \Delta h + \Delta d$) that protrudes above an alkanethiol monolayer (Figure 3a). In this two-layer model, the transconductance of a given layer is $G_i = \text{G}_0\ \text{exp}(-\Gamma_i t_i)$, where G_0 is the contact conductance, Γ_i is the decay constant, and t_i is the layer thickness, and the overall junction transconductance is the sum of layer transconductances $G = G_{\text{gap}}G_{\text{molecule}}$. STM images obtained in constant current mode constrain the junction transconductance to a constant value for the entire image ($G_{\text{C11}}G_{\text{gap}} = G_{\mathbf{2}}G_{\text{gap}}$). By applying the simplifying assumptions that the characteristics of the gap (G_{air} and α) and the contact conductance (G_0) are constant for the two molecules,[17] we are able to solve for $\beta_{\mathbf{2}}$ in terms of the apparent height of the molecule:

$$\beta_{\mathbf{2}} = [\beta_{\text{C11}}h_{\text{C11}} - \alpha(\Delta\text{STM} - \Delta h)]/h_{\mathbf{2}} \qquad (1)$$

Table 1 lists β values for **2**, along with a comparison to OPE (Figure 3b), a well studied fully organic analogue.[10,16,18]

Table 1. Molecular Length, Apparent Height, and β Values[19,20]

molecule	length (Å)	STM apparent height (Å)	β (Å^{-1})
C11	12.5	0	1.2
OPE	20.2	4.3	1.03 ± 0.13
2 (S to final C)	22.4	7.8	0.88 ± 0.12
2 (S to final Ru)	18.6	7.8	0.59 ± 0.08

As Table 1 shows, the 20.2 Å dithiol OPE molecule yields a β of 1.03 ± 0.13 Å^{-1}, which is consistent with previous observations on monothiol OPE.[11,16] There are two values presented for compound **2**, reflecting inherent uncertainty in the STM experiment since we do not know from which atoms in **2** the tunneling is occurring. Tunneling from the final phenyl carbon yields a β of 0.88 ± 0.12 Å^{-1}, while tunneling from the final Ru atom drops β to 0.59 ± 0.08 Å^{-1}. Although the extended conjugation along the Ru−Ru−(C≡CC$_6$H$_4$)$_2$−S linkage is very similar to that of OPE, introducing Ru$_2$(ap)$_4$ at the end of the molecule deceases β by a minimum of 15%.

We have successfully synthesized $\text{Ru}_2(\text{ap})_4[\sigma\text{-}(\text{C}{\equiv}\text{CC}_6\text{H}_4)_n\text{SCH}_2\text{CH}_2\text{SiMe}_3]$ and measured the electronic transport properties of **2** while embedded in a C11 thiol matrix on a gold substrate. CV measurements reveal the presence of low potential redox states, demonstrating the successful addition of an electrochemical "handle" into a molecular wire. STM measurements show that **2** yields a β that is at least 15% and possibly 43% lower than the fully organic OPE molecule, suggesting that the introduction of a Ru$_2$ fragment enhances the transconductance of molecular wires, possibly through decreasing the E_g. Our results suggest that it may be possible to improve the performance of molecules for molecular electronics through rational design and molecular engineering. This is a key finding if molecular electronics is to fulfill its promise.

Acknowledgment. Support for this work comes from the Defense Advanced Research Program Agency (to J.G.K. and R.S.) and the National Science Foundation (CHE0242623 to T.R.).

Supporting Information Available: Synthesis and characterizations of compounds **1** and **2** (PDF), and X-ray crystallographic file in CIF format for the structure determination of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA052604E