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Length-Dependent Conductance of Conjugated Molecular Wires Synthesized by Stepwise "Click" Chemistry

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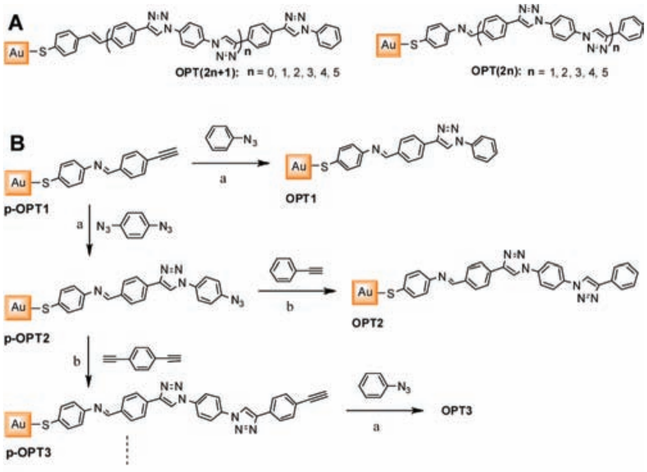
Received April 16, 2010; E-mail: frisbie@cems.umn.edu

Recently, we and others have demonstrated length-dependent conduction measurements on assemblies of very long (7−40 nm) conjugated molecular wires connected to metal electrodes.[1−3] Systematic examination of the length dependence of the wire resistance reveals that above a critical length, ∼4 nm for oligoarylamine wires, the conduction mechanism switches from tunneling to hopping,[1,2] as is anticipated from theory and prior photoinduced electron transfer studies.[4−7] To further develop understanding of molecular charge transport, particularly in the less well explored hopping regime, it is necessary to examine conduction in wires with different molecular architectures. However, to date there are very few methods for synthesis of long (>4 nm) π-conjugated wires bonded to metal electrodes.[3,8] The development of new wire synthesis protocols in which both wire length and bonding architecture are manipulated precisely will enhance opportunities for systematic examination of structure−transport relationships in molecules.

In this communication we report a reliable and efficient method to prepare conjugated molecular wires connected between metal electrodes using stepwise Cu(I)-catalyzed azide alkyne cycloaddition. The reaction, known as "click chemistry",[9] takes place in mild conditions and shows a high regioselectivity and a great tolerance to functional groups. Previous research results have demonstrated that click methodology is applicable for the modification of azide or alkyne terminated self-assembled monolayers (SAMs)[10,11] and for the in situ synthesis of molecular wires to bridge nanogaps.[12] Here we employ click cycloaddition to prepare oriented, conjugated molecular wires bonded to a metal surface with controlled lengths up to 10 nm. The wires we have produced, oligophenylenetriazole (OPT) wires, have an all-aromatic backbone structure and are shown in Figure 1A. Their $I-V$ characteristics were measured by conducting probe atomic force microscopy (CP-AFM) and reveal a transition in direct current (DC) transport from tunneling to hopping with increasing molecular length, but with higher estimated conductivities than we have reported previously for oligoarylimine wires synthesized using Schiff base chemistry.[1,2]

Figure 1B shows the synthetic route toward OPT wires and their precursors (p-OPT). The growth of OPT wires on Au surfaces starts with a SAM of p-OPT1, the preparation of which is detailed in section 3.1, Supporting Information. p-OPT1 converts to p-OPT2 by undergoing the click cycloaddition with 20 mM 1,4-diazidobenzene in a 2.5:1 ethanol/H_2O solution containing 2 mol % copper(II) sulfate pentahydrate and 15 mol % sodium ascorbate as catalysts. p-OPT3 is prepared by the sequential cycloaddition on p-OPT2 with 20 mM 1,4-ethynylbenzene in acetonitrile/H_2O (2.5:1), catalyzed by the same system in the previous step. Alternate addition of 1,4-diazidobenzene and 1,4-diethynylbenzene results in the growth of p-OPT wires, with wire length controlled by the number of added building blocks, as shown in Figure 1B. Finally, each p-OPT wire terminated with alkyne or azide groups reacts with phenylazide or phenylacetylene, respectively, to produce the corresponding OPT wire. The consistent end-cap phenyl group of each OPT wire ensures systematic and reproducible electrical characterization of the whole OPT series. Before each synthesis step, each p-OPT or OPT film was thoroughly rinsed with absolute ethanol and DI water and dried in a stream of N_2 to eliminate physically adsorbed chemicals.



a: $CuSO_4 \cdot 5H_2O$ 2 mol%, Sodium Ascorbate 15 mol%, EtOH/H_2O (2.5:1), RT 12 ~ 18 h
b: $CuSO_4 \cdot 5H_2O$ 2 mol%, Sodium Ascorbate 15 mol%, CH_3CN/H_2O (2.5:1), RT 18 ~ 24 h

Figure 1. (A) Molecular structures of OPT wires. (B) Synthetic route to p-OPT and OPT monolayers on Au surfaces.

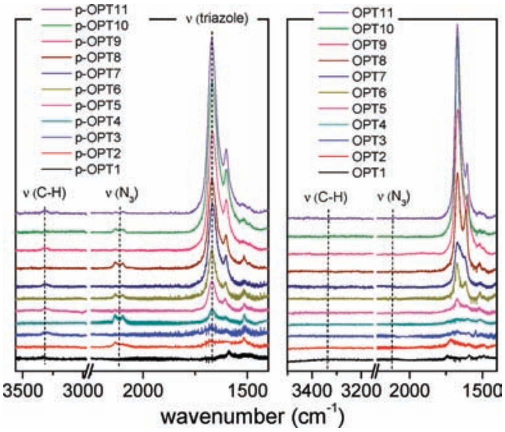


Figure 2. RAIRS spectra of p-OPT (left) and OPT (right) monolayers. Vertical dashed lines indicate positions of the stretches of terminal alkyne (≡C−H), azide (N_3), and triazole respectively.

Both p-OPT and OPT SAMs were comprehensively characterized by reflection absorption Fourier transform infrared spectroscopy (RAIRS), ellipsometry, and X-ray photoelectron spectroscopy (XPS). The RAIRS spectra of all p-OPT and OPT SAMs are shown

10.1021/ja103239b © 2010 American Chemical Society

in Figure 2. The spectra of alkyne-terminated p-OPT SAMs show a characteristic peak at 3320 cm^{-1} ($\equiv$C—H stretching),[12,13] while those of azide-terminated p-OPT SAMs exhibit a doublet peak centered at 2120 cm^{-1} (N_3 asymmetric stretching).[14] The alternate appearance and disappearance of these two peaks in p-OPT wires verifies the completion of click cycloaddition to all exposed reactive end groups. In addition, the peak intensities of the triazole stretching mode (1670 cm^{-1}) and benzene ring vibration (1610 cm^{-1}) increase gradually upon repeated click cycloaddition, as expected. After all the wires were end-capped, both azide and alkyne stretching peaks disappeared in the spectra of OPT SAMs (Figure 2, right). The thicknesses of OPT SAMs measured by ellipsometry and XPS increase upon stepwise elongation of the molecular wires (section 3.4, Supporting Information). Based on the ellipsometry results we estimate that the molecules are tilted on average by ~30° with respect to the surface normal.

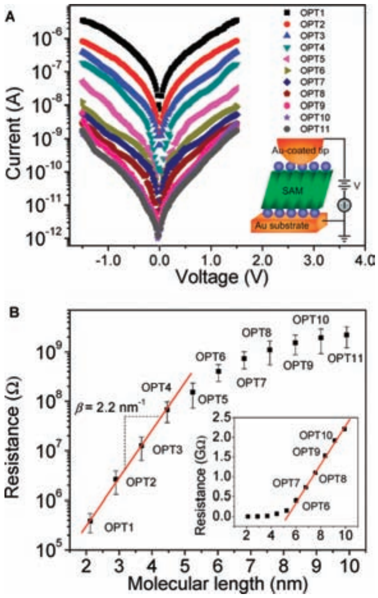


Figure 3. Electrical measurements of molecular wires by CP-AFM. (A) Semilog plot of the average current of 20 $I-V$ curves for all Au/OPT wire/Au junctions. $I-V$ curves were obtained over ±1.5 V at a load of 2 nN on the tip contact. Inset: A Au-coated tip was brought into contact with an OPT SAM on Au surface. (B) Semilog plot of R versus L for the Au/wire/Au junctions. Each data point is the average differential resistance obtained from 20 $I-V$ curves in the range of ±0.1 V. Error bars represent 1 standard deviation. Straight line is a linear fit to the short wires according to eq 1. The inset is a linear plot of R versus L. Straight line is a linear fit to the long wires.

We examined the length-dependent conduction of the OPT wires using CP-AFM with a Au-coated tip (Figure 3A inset). Current−voltage ($I-V$) sweeps generally yielded sigmoidally shaped curves; semilog plots of I versus V for each OPT wire in the Au/wire/Au junction are shown in Figure 3A. The current decreases with increased wire length, and the changes for short wires (OPT 1−5) are much larger than those for long wires (OPT 6−11). The resistances R shown in Figure 3B are low voltage resistances determined over a small voltage range (±0.1 V) within which each $I-V$ curve is linear. R increases exponentially with molecular length L for short molecules (OPT 1−4), as described by the nonresonant tunneling equation

$$R = R_0 \exp(\beta L) \tag{1}$$

where R_0 is the effective contact resistance and β is the tunneling attenuation factor. The β value obtained from a linear fit is 2.2 nm^{-1}, smaller than that obtained in previously reported oligoarylimine wires,[1,2] suggesting more efficient electron tunneling through the all-aromatic backbones of the OPT molecules. For long wires (OPT 5 and longer), the resistances have a much weaker length dependence. The linear relationship of R versus L (Figure 3B inset) for the long wires is consistent with hopping transport. Furthermore, the clear transition in the length dependence of resistance between 4 and 5 nm is consistent with our previous observations in oligoarylimine wires of a change in transport mechanism from tunneling to hopping.[1,2]

In summary, stepwise click cycloaddition represents an efficient method to prepare long conjugated molecular wire SAMs on Au surfaces for conduction measurements. The reaction proceeds cleanly, and it is reasonable to expect that it can be used to introduce a variety of functionalities and bonding architectures into the wire backbones. The all-aromatic conjugated molecules reported here exhibit similar electrical characteristics to other conjugated wire molecules, with a clear transition from tunneling to hopping transport as wire length increases. Future work will focus on exploring the relationship between molecular architectures and electron transport in the hopping regime.

Acknowledgment. This work is supported by the National Science Foundation (CHE-0616427). Part of this work was carried out in the Institute of Technology Characterization Facility, University of Minnesota.

Supporting Information Available: Detailed experimental procedures and characterization of all SAMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA103239B