

First Optically Active Molecular Electronic Wires

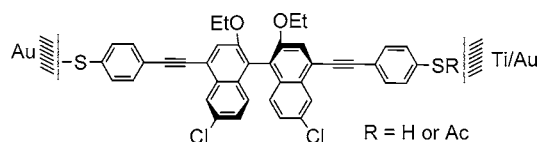
Yuliang Zhu,[†] Nadine Gergel,[‡] Nabanita Majumdar,[‡] Lloyd R. Harriott,[‡]
John C. Bean,[‡] and Lin Pu^{*,†}

Department of Chemistry and Department of Electrical and Computer Engineering,
University of Virginia, Charlottesville, Virginia 22904-4319

lp6n@virginia.edu

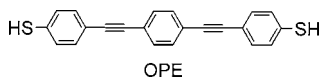
Received July 20, 2005

ABSTRACT



The optically active molecular electronic wires (*S*- and *R*-7) containing an oligo-arylene-ethynylene structure and a chiral 1,1'-binaphthyl unit are synthesized. These molecules are incorporated into nanowell devices by self-assembly on the gold surface. In the nanowell devices, the median currents from the molecules containing both *S* and *R* enantiomers are significantly smaller than those from the pure *S* or *R* molecule. Compounds (*R*- and *S*-7) are also less conductive than the fully conjugated oligo-phenylene-ethynylene-thiol molecules.

Self-assembly of conjugated organic thiol molecules, such as the oligo-phenylene-ethynylene-dithiol (OPE), on the surface of gold has allowed the study of electron transport at the molecular scale.^{1,2} Application of these molecular



electronic wires in constructing novel electronic devices is under active investigation. Self-assembled functional organic molecules on solid surfaces have also been used as sensors

for various substrate detections.^{3,4} In our laboratory, we are interested in developing chiral optical and electrical sensors for enantioselective recognition. Such sensors will find applications in the high throughput assay of chiral organic compounds.^{5,6} Thus, incorporation of chirality into the OPE molecules to construct chiral molecular electronic devices should be of both practical and fundamental significance. Herein, we report the synthesis of the first optically active molecular electronic wires and the study of their optical and electrical properties.

We have used the axially chiral 1,1'-bi-2-naphthol (BINOL) as the starting material to make various novel chiral

[†] Department of Chemistry.

[‡] Department of Electrical and Computer Engineering.

(1) (a) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. *J. Am. Chem. Soc.* **1995**, *117*, 9529–9534. (b) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705–1707.

(2) (a) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550–1552. (b) Lewis, P. A.; Inman, C. E.; Yao, Y.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 12214–12215. (c) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem.–Eur. J.* **2001**, *7*, 5118–5134.

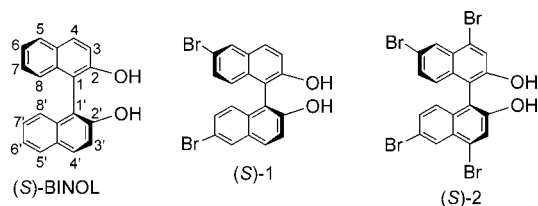
(3) (a) Motesharei, K.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 11306–11312. (b) Rickert, J.; Weiss, T.; Gopel, W. *Sens. Actuators, B: Chem.* **1996**, *31*, 45–50. (c) Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957–1974. (d) Chaki, N. K.; Vijayamohanam, K. *Biosens. Bioelectron.* **2002**, *17*, 1–12.

(4) Chiral recognition using self-assembled materials on a solid surface: (a) Paolesse, R.; Monti, D.; La Monica, L.; Venanzi, M.; Froiio, A.; Nardis, S.; Di Natale, C.; Martinelli, E.; D'Amico, A. *Chem.–Eur. J.* **2002**, *8*, 2476–2483. (b) He, J. X.; Sato, H.; Yang, P.; Yamagishi, A. *Electrochem. Commun.* **2003**, *5*, 388–391.

(5) Pu, L. *Chem. Rev.* **2004**, *104*, 1687–1716.

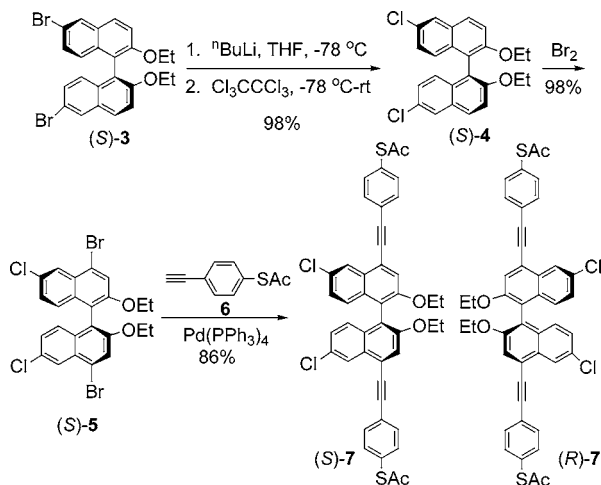
(6) (a) Pugh, V.; Hu, Q.-S.; Pu, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3638–3641. (b) Li, Z.-B.; Lin, J.; Pu, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1690–1693.

molecules and macromolecules for diverse applications.^{5–10} Previously, it was found that BINOL could be specifically brominated at the 6,6'-positions to give (*S*)-**1**.¹¹ We later found that when the 6,6'-positions of BINOL were occupied, additional bromination occurred at the 4,4'-positions to give the tetrabromo-BINOL (*S*)-**2**.¹² Preparation of (*S*)-**1** and (*S*)-**2** makes it possible to further derivatize BINOL at the 6,6'- and 4,4'-positions, and chiral materials of diverse structures have been made from these compounds.



To synthesize an optically active molecular electronic wire, we planned to introduce the conjugated phenyleneethynylene units to the 4,4'-positions of BINOL. Lee and Lin reported the synthesis of the 4,4',6,6'-tetrahalogenated BINOL compound (*S*)-**5** in which the 6,6'-dibromo atoms are replaced with two chlorines, and they used this compound as the precursor to prepare 4,4'-substituted BINOL-based materials (Scheme 1).¹³ A modified procedure is adopted here. As shown in Scheme 1, compound (*S*)-**3**, prepared by bromi-

Scheme 1. Synthesis of the Chiral Conjugated Molecules (*S*)- and (*R*)-**7**



- (7) Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494.
 (8) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. R.; Pu, L. *Macromolecules* **1996**, *29*, 1082–1084.
 (9) Huang, W.-S.; Hu, Q.-S.; Zheng, X.-F.; Anderson, J.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4313–4314.
 (10) Yu, H.-B.; Hu, Q.-S.; Pu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6500–6501.
 (11) Sogah, G. D. Y.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3035–3042.
 (12) Hu, Q.-S.; Pugh, V.; Sabat, M.; Pu, L. *J. Org. Chem.* **1999**, *64*, 7528–7536.

nation and alkylation of (*S*)-BINOL, was treated with ⁿBuLi at –78 °C followed by the addition of hexachloroethane to give the 6,6'-dichloro-BINOL (*S*)-**4**. Bromination of (*S*)-**4** led to the formation of (*S*)-**5**. Because of the much greater reactivity of an aryl bromide than that of an aryl chloride in a cross-coupling reaction, the Sonogashira coupling of (*S*)-**5** with the thioacetyl phenyl acetylene **6**¹⁴ gave the desired compound (*S*)-**7**.^{13b} The specific optical rotation of (*S*)-**7** was $[\alpha]_D -60.1$ ($c = 1.0$, CH₂Cl₂). The enantiomer of this molecule, (*R*)-**7**, was synthesized by starting from (*R*)-BINOL. The acetyl groups of compounds (*S*)- and (*R*)-**7** can be removed in situ under acidic conditions to form chiral molecular nanowires during the preparation of the self-assembled monolayers on gold. The distance between the two ending sulfur atoms of these molecules is calculated to be 2.4 nm.

We compared the optical properties of the chiral conjugated molecules with the linear achiral oligo-phenyleneethynylene molecule **8**.^{2c} Figure 1 gives the UV spectra of

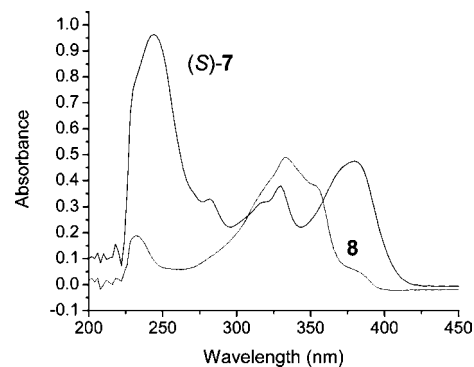
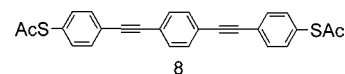


Figure 1. UV spectra of (*S*)-**7** and **8** in methylene chloride (10^{–6} M).

(*S*)-**7** and **8** in methylene chloride. Previously, we demonstrated that in the 1,1'-binaphthyl-based conjugated materials there is no conjugation across the 1,1'-bond of the 1,1'-binaphthyl unit because of its preferred orthogonal geometry.⁷ Therefore, the UV absorptions of (*S*)-**7** should be due to the half part of this molecule that can achieve a planar conjugation. Unlike (*S*)-**7**, the π electrons of **8** are fully conjugated. Comparison of their UV spectra demonstrates that the naphthalene unit in the half part of (*S*)-**7** provides more effective conjugation than a diphenylacetylene unit in **8**.



The fluorescence spectra of (*S*)-**7** and **8** are provided in Figure 2. Compound (*S*)-**7** displays a longer wavelength

- (13) (a) Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554–4555.
 (b) Cui, Y.; Ewans, O. R.; Ngo, H. L.; White, P. S.; Lin, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 1159–1162. (c) Lee, S. J.; Hu, A.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 12948–12949.
 (14) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376–1387.

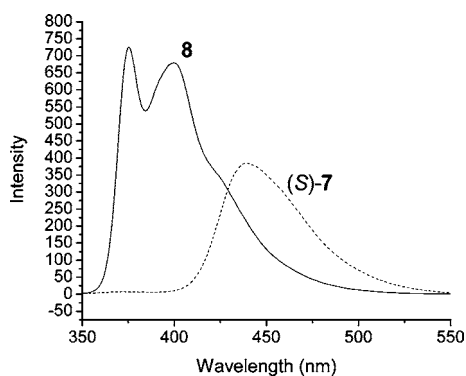


Figure 2. Fluorescence spectra of (*S*)-**7** and **8** in methylene chloride (10^{-5} M).

emission than **8**. The emission maximum of (*S*)-**7** is at 439 nm while it is excited at 330 nm. Compound **8** gives a more vibrational structure in its fluorescence spectrum with λ_{max} at 376, 400, and 424 (sh) nm while it is excited at 334 nm.

The circular dichroism spectra of the two enantiomers (*S*)- and (*R*)-**7** in methylene chloride are given in Figure 3 which

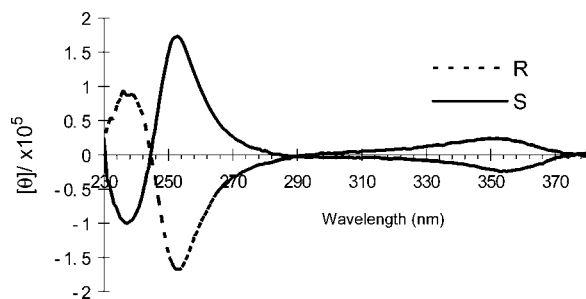


Figure 3. Circular dichroism spectra of (*S*)- and (*R*)-**7** in methylene chloride (10^{-5} M).

exhibits the expected mirror image relation. The positive and negative Cotton effects centered at ca. 245 nm can be attributed to the exciton coupling of the two axially chiral naphthalene units. The long wavelength positive and negative Cotton effects may be attributed to the extended conjugation with the incorporation of the 4,4'-arylethynylene units.

We studied the electrical transport properties of the chiral conjugated molecules (*S*)- and (*R*)-**7** in a nanowell test device as shown in Figure 4. This device consisted of a silicon wafer that was patterned with gold and covered with silicon dioxide. A focused ion beam (FIB) was used to mill a well down through the silicon dioxide. Monolayers of the desired molecules self-assembled on the gold surface were capped with a top layer of titanium and gold. The top and bottom gold layers were then electrically probed, a voltage was applied between them, and the corresponding current through the monolayer was measured. Greater details of this nanowell

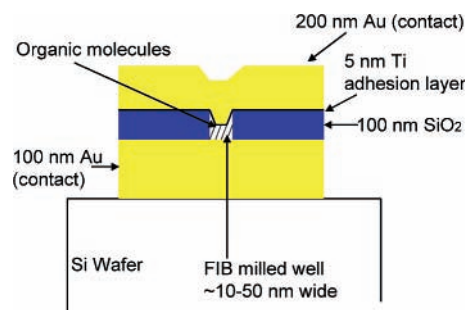


Figure 4. Nanowell device.

device are described elsewhere.¹⁵ We used an HP 4145 B probe station to test the room temperature electrical characteristics of the molecules in the device. Prior to testing the chiral molecules for this work, we established the effectiveness of the nanowell device by testing molecules with well-known electrical characteristics.¹⁵

The chiral conjugated molecules were first dissolved in ethanol in the presence of sulfuric acid which removed the acetyl protecting groups in situ. Then, the chips with the exposed nanowells were placed in the chiral molecule solution for a minimum of 48 h. The molecules self-assembled because of bonding between the thiol end groups and the exposed gold bottom of the nanowell (Figure 5).

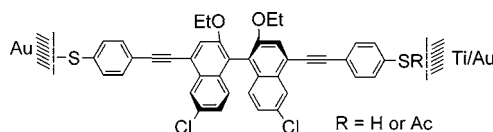


Figure 5. Optically active molecular electronic wire in the nanowell.

After assembly of the molecules, the chips were removed and rinsed with THF and titanium and gold were evaporated to form a top contact.

We first tested the electrical properties of (*R*)-**7**. The current–voltage (*I*–*V*) curves of 67 out of the 80 devices tested for this type showed either clear electrical opens, due to the top electrode not making contact to the molecule, or electrical shorts, due to the top contact shorting to the bottom contact. The other 16% of devices tested showed electrical characteristics that were exponential and could be repeated. This percent of “working” devices is consistent with percentages observed for testing other molecules in the nanowell.¹⁵ The *I*–*V* curves were occasionally asymmetric on the positive or negative voltage side and showed permanent electrical breakdown when voltages with magnitudes of 2.5

(15) Mjumdar, N.; Gergel, N.; Routenberg, D.; Harriott, L. R.; Bean, J. C.; Li, B.; Pu, L.; Yao, Y.; Tour, J. M. *J. Vac. Sci. Technol., B* **2005**, *23*, 1417–1421.

V and higher were applied. The median current value at 1.5 V was 1.3 nA. An example of the I - V characteristics observed is shown in Figure 6a.

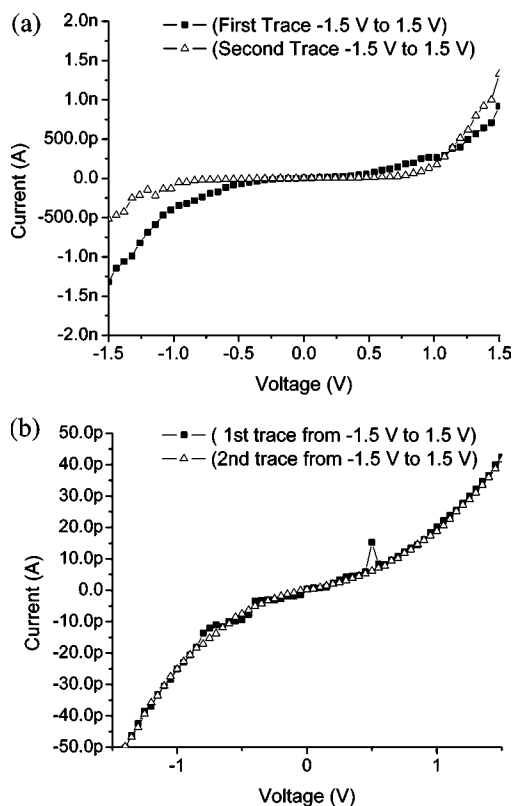


Figure 6. (a) I - V plot of (R) -7 in the nanowell. (b) I - V plot of the devices containing 80% R and 20% S in the nanowell.

The behaviors of (S) -7 were very similar to those of its enantiomer (R) -7. Generally asymmetric, exponential, and repeatable I - V curves were observed from 10 out of the 48 devices tested electrically (about 21% yield). The devices broke down when voltages similar to those for (R) -7 were applied. The median current at 1.5 V was 3.5 nA. Yet, the median currents for the pure (R) - and (S) -7 were about one order of magnitude lower than the median current we found for simple dithiol OPE molecules. The nonplanar binaphthyl unit of (S) -7 which does not allow this molecule to be fully conjugated should be one of the important factors for its lower conductivity.

We also tested the devices that were composed of various enantiomeric compositions of (R) - and (S) -7: 80% R and 20% S , 50% R and 50% S , and 20% R and 80% S . The samples with the three different enantiomeric compositions produced working devices in yields of 25%, 12.5%, and 19%, respectively. The characteristics of the I - V curves were similar to those of the pure R and pure S molecules, except in current magnitudes: the median current magnitudes for the three compositions were 43 pA, 89 pA, and 62 pA, respectively. Despite the large range of currents inherent to the nanowell device, it is clear that the optically pure compound exhibits greater conductivity than the mixtures. This large range of current magnitudes has been observed for other molecules tested in the nanowell device and may be due to variations in device well sizes.¹⁶ An example of the I - V characteristics observed for the mixture containing 80% R and 20% S is shown in Figure 6b.

In summary, the first optically active molecular electronic wires (S) - and (R) -7 containing an oligo-arylene-ethynylene structure and a chiral 1,1'-binaphthyl unit are synthesized. These molecules are incorporated into nanowell devices by self-assembly on the gold surface. In the nanowell devices, the self-assembled pure S and R enantiomers exhibit similar exponential and repeatable I - V curves. However, the median currents from the molecules containing both S and R enantiomers are significantly smaller than those from the pure S or R molecules. This could be attributed to possibly very different packing structures between the homochiral and heterochiral molecules. Thus, the chirality of these chiral nanowires has a strong influence on their electrical transport properties. In addition, compounds (R) - and (S) -7 containing the nonplanar chiral binaphthyl unit are also less conductive than the fully conjugated oligo-phenylene-ethynylene-thiol molecules. The chiral electronic devices will be used to interact with various chiral organic molecules to explore the potential of these materials in enantioselective sensing.

Acknowledgment. We thank the National Science Foundation (NIRT 0210585) and DARPA/ONR MoleApps program (N000140410706) for supporting this work.

Supporting Information Available: Synthesis and characterization of (S) -4 and (S) -7 and the UV absorption data of **8**. Comparison of the currents of the homochiral and heterochiral molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL0517168

(16) Gergel, N.; Majumdar, N.; Keyvanfar, K.; Swami, N.; Harriott, L. R.; Bean, J. C. *J. Vac. Sci. Technol., A* **2005**, *23*, 880–885.