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*Citation for published version (APA):*
Durkut, M., Mas-Torrent, M., Hadley, P., Jonkheijm, P., Schenning, A. P. H. J., Meijer, E. W., George, S. J., & Ajayaghosh, A. (2006). Electrical transport measurements on self-assembled organic molecular wires. *Journal of Chemical Physics*, *124*(15), 154704-1/6. https://doi.org/10.1063/1.2186312

*DOI:*
10.1063/1.2186312

*Document status and date:*
Published: 01/01/2006

*Document Version:*
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

*Please check the document version of this publication:*

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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THE JOURNAL OF CHEMICAL PHYSICS **124**, 154704 (2006)

# Electrical transport measurements on self-assembled organic molecular wires

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(Received 28 September 2005; accepted 16 February 2006; published online 17 April 2006)

The electrical properties of supermolecular assemblies of oligo(*p*-phenylene vinylene) were studied. These materials self-assemble into well-defined cylindrical structures in solution with lengths in the range of 100 nm – 10 $\mu$m and diameters between 5 and 200 nm. Atomic force microscopy showed that by adjusting the concentration, either individual molecular wires or a dense film could be deposited. The molecular wires showed poor electrical conduction. Several tests were performed that show that it was the molecular wires themselves, not the contacts, that limit the conductivity. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2186312]

## I. INTRODUCTION

Under suitable conditions, certain molecules will form well-defined one dimensional assemblies that can conduct electricity as molecular wires. Recently, films of such assemblies have been used to make field effect transistors,[1] light emitting diodes,[2] and solar cells.[3] Here we investigate samples consisting of just a few of these molecular wires to try to understand their electronic transport properties and to evaluate if individual wires could be used as electronic components. Using chemical synthesis to produce electronic components is appealing because if electronic components such as diodes or transistors could be synthesized chemically, the position of every atom in the device would be known and the devices could be optimized on the atomic scale. Chemical synthesis is also a process that can be scaled up easily. Much of the effort along these lines has so far focused on making devices that are smaller than conventional silicon transistors. Unfortunately, small molecular transistors have the same problems as small silicon transistors: low signal gain, low current drive, and large leakage currents. The problem seems to be that they are too small to be good transistors. One strategy to overcome the problem of poor performance in small molecular transistors is to try to make big molecular transistors. Supermolecular chemistry is ideally suited for making structures with sizes of 10 – 100 nm. This is the size range that is most suitable for electronic applications. For an overview of supermolecular electronics, see Ref. 4.

In the experiments described here, molecular wires that spontaneously formed in solution were drop cast on metal electrodes spaced 200 nm apart. Figure 1 shows the device configuration. The molecular wires we investigated were oligo(*p*-phenylene vinylene) (OPV) with hydrogen bonding moieties of variable strength, MOPV$_4$, OPVT$_4$, or bishydroxy OPV$_3$ (Fig. 2). Previous electrical measurements of dense networks of these wires using widely spaced electrodes indicated that the wires were poor electrical conductors.[1] Those experiments could not exclude the possibility that the conductivity was limited by poor interwire conduction. In the present experiment, the electrodes are closer together than the wires are long. This excludes the possibility that the conductivity measured is limited by interwire conduction. To induce charge carriers in the wires, a gate voltage that induced fields as high as $4 \times 10^5$ V/cm was applied. Nevertheless, no appreciable current could be measured in the wires. Great care was taken to show that the conductivity was not limited by the contacts to the metal

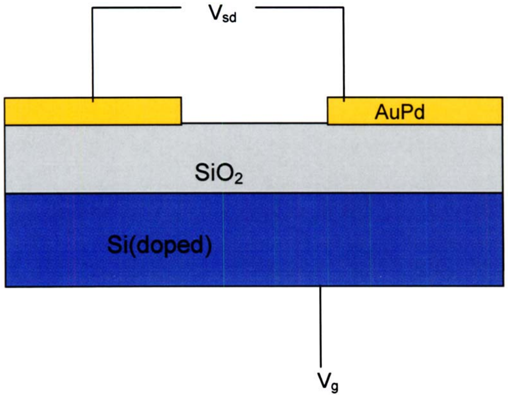

FIG. 1. The device configuration. Electrodes are of Au$_{60}$Pd$_{40}$ and Ti. The gap between the electrodes is 200 nm. The thermally grown SiO$_2$ of 200 nm is used as a gate oxide and the doped Si substrate is used as a gate.

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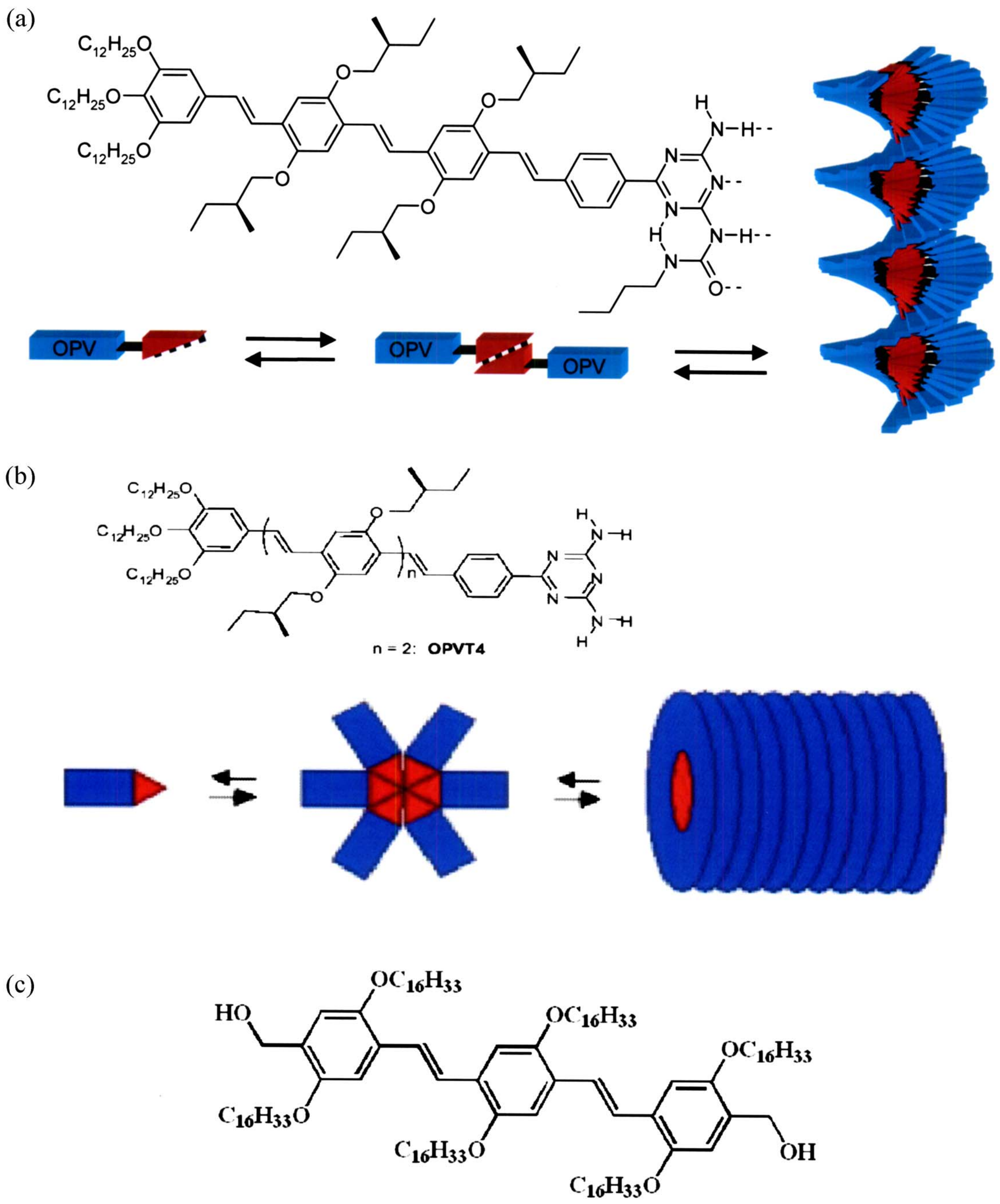

FIG. 2. (a) The monomer MOPV$_4$ [mono-tetra($p$-phenylene vinylene)] and a schematic representation of a helical stack formed by this molecule. The bars represent MOPV$_4$ and the triangles represent the hydrogen-bonding urideo-triazine units. (b) The monomer OPVT$_4$ [oligo($p$-phenylene vinylene)-triazine] and a schematic representation of the helical stack formed by this monomer. (c) The bishydroxy OPV$_3$ oligomer. These monomers self-assemble into sheets that then probably roll up into supramolecular tapes.

electrodes. Both large bias voltage experiments and contactless electrostatic force microscopy (EFM) measurements[5–8] were performed to investigate the contacts.

## II. EXPERIMENT

### A. Materials

MOPV$_4$ wires were constructed from OPV derivatives with a ureido-triazine head group and a trialkoxy wedge [Fig. 2(a)]. In heptane, the monomers dimerize by the formation of four hydrogen bonds between two head groups. The dimers then stack in a helical structure to form wires 5.2 nm in diameter and several microns long depending on the concentration. The mechanism driving the formation of the wires is presumed to be hydrogen bonding and $\pi$-$\pi$ stacking. Circular dichroism spectroscopy and small angle neutron scattering measurements confirm that helical wires are formed.[9,10]

The basic unit of the OPVT$_4$ wires [Fig. 2(b)] is very similar to that of MOPV$_4$. The difference is that the OPVT$_4$ monomers bear a hydrogen-bonding group that forms weaker hydrogen bonds. In heptane, six OPVT$_4$ monomers come together to form hexameric $\pi$-conjugated rosettes. These ro-

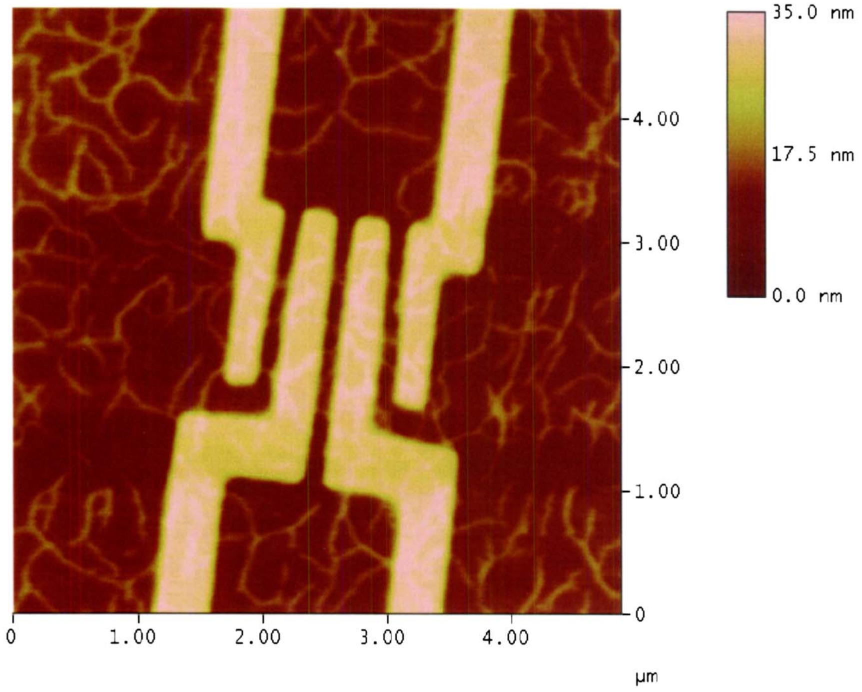

FIG. 3. An AFM image of $MOPV_4$ wires lying across $Au_{60}Pd_{40}$ electrodes.

settes then self-assemble into helical wires with a diameter of 7 nm and length of several microns. The structure of these wires has been investigated by scanning tunneling microscopy, UV-vis, fluorescence, and circular dichroism spectroscopy.[11]

The third wire investigated was bishydroxy $OPV_3$. This $OPV_3$ derivative has two hydroxy (OH) end groups and long alkyl side chains [Fig. 2(c)]. Bishydroxy $OPV_3$ monomers self-assemble into sheets via hydrogen bonds and van der Waals interactions between the long alkyl tails. The sheets then probably form supramolecular tapes. The tapes are stabilized by $\pi$-$\pi$ interactions and additional hydrogen-bond interactions. There is a large variation in the length and the diameter of the tubes. They can be micrometers long and several hundred nanometers in diameter.[12,13]

### B. Device preparation

Closely spaced metal electrodes were made by electron-beam lithography. A double resist layer of poly(methyl methacrylate) (PMMA) was spun on a boron doped ($5 \times 10^{14}$ $cm^{-3}$) silicon wafer with a 200 nm thick thermally grown oxide. The pattern was written with an electron-beam pattern generator [EBPG5 HR 100 kV field emission gun (FEG)]. Metal electrodes of $Ti/Au_{60}Pd_{40}$ were evaporated at liquid nitrogen temperature to ensure a smooth surface and lift-off was done in acetone. A four-probe electrode pattern was used where the width and the spacing of the electrodes were 200 nm (Fig. 3).

Wires dissolved in heptane or toluene were cast in drops between 5 and 10 $\mu$l onto substrates with prefabricated electrodes. The solvent was allowed to evaporate, leaving wires on the surface. The concentration was chosen to produce well-separated wires. To achieve a dense covering of wires, higher concentrations were used. It was observed that the wires decomposed on Au electrodes but they maintained their form on $SiO_2$ or $Au_{60}Pd_{40}$ electrodes. After the solvent was allowed to evaporate, electrical transport measurements were made at room temperature in a microscope probe station in ambient. The electronic measurement system could measure resistances up to 1 TΩ. The samples were inspected by atomic force microscopy (AFM) before and after the electrical measurements were performed, using a Digital Instruments (DI) AFM (Nanoscope IV) in tapping mode. The same AFM was also used for EFM measurements.

## III. RESULTS

### A. Transport measurement

Figure 3 is an AFM image of the electrodes with $MOPV_4$ wires lying over it when drop cast from heptane (0.02 mg/ml). Electrical measurements were performed applying a bias up to ±30 V. For voltages above 30 V, the electrodes were destroyed by dielectric breakdown with or without wires lying over them. To try to increase the number of charge carriers in the wires, a voltage of up to ±80 V was applied to the silicon substrate. Measurements were performed on 20 samples, but none showed any electrical conduction. When a 75 nm thick layer of the wires was deposited, currents on the order of $10^{-15}$ A/nm were measured.[1] This current density is too low to be measured in individual wires.

A solution of $OPVT_4$ with a concentration of 0.023 mg/ml in heptane gave a network of wires on the electrodes [Fig. 4(a)]. The measurements on these networks did not show any electrical conduction up to bias voltage of ±8 V. No gate dependence was observed up to ±80 V. Electrical measurements performed on electrodes covered with a film of $OPVT_4$ wires were also not conducting.

Bishydroxy $OPV_3$ wires were drop cast on electrodes with different concentrations. Figure 4(b) shows an AFM

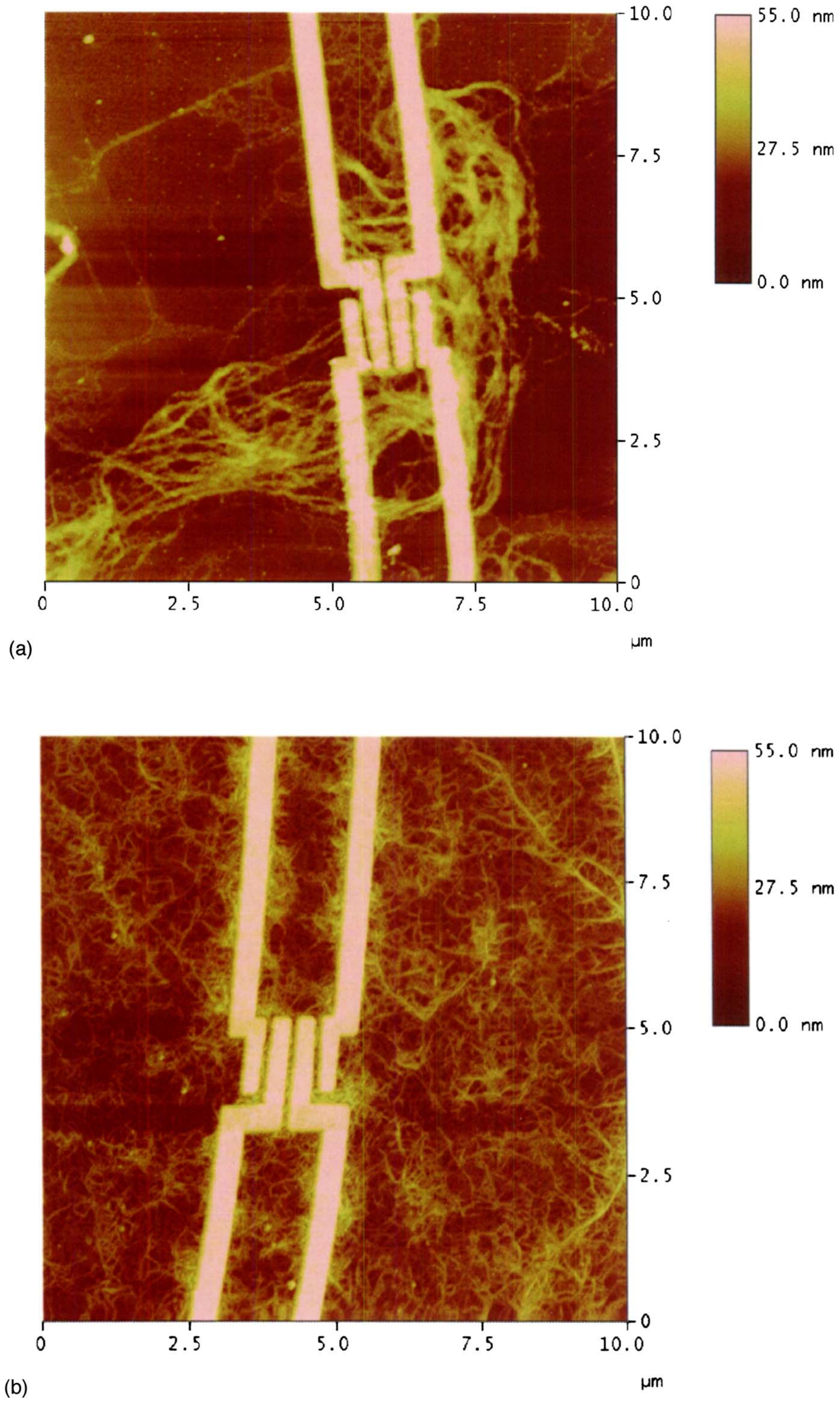

FIG. 4. (a) An AFM image of the $OPVT_4$ wires on the $Au_{60}Pd_{40}$ electrodes. The wires were drop cast from heptane (0.23 mg/ml). (b) An AFM image of bishydroxy $OPV_3$ wires on the electrodes. The wires were drop cast from toluene (0.05 mg/ml).

image of a network of wires on the electrodes when drop cast from toluene (0.05 mg/ml). Electrical transport measurements on this electrode and several other electrodes showed poor conduction with currents of a few picoamperes, just above the noise. Bias voltages up to ±8 V were applied. There was no gate dependence up to gate voltage of ±80 V. Measurements performed on electrodes covered with a dense film of wires showed the same *I*-*V* characteristics and no gate effect.

## B. Contacts

The reason that so little current was measured in these experiments could either be that the contacts are poor or the wires are not conducting. The $MOPV_4$ and $OPVT_4$ wires are coated by alkyl chains that were included to make the constituents of the wires soluble. These alkyl chains are known to be poor conductors. However, separate measurements on alkyl chains show that if most of the voltage that was applied dropped over the alkyl chains, much higher currents should

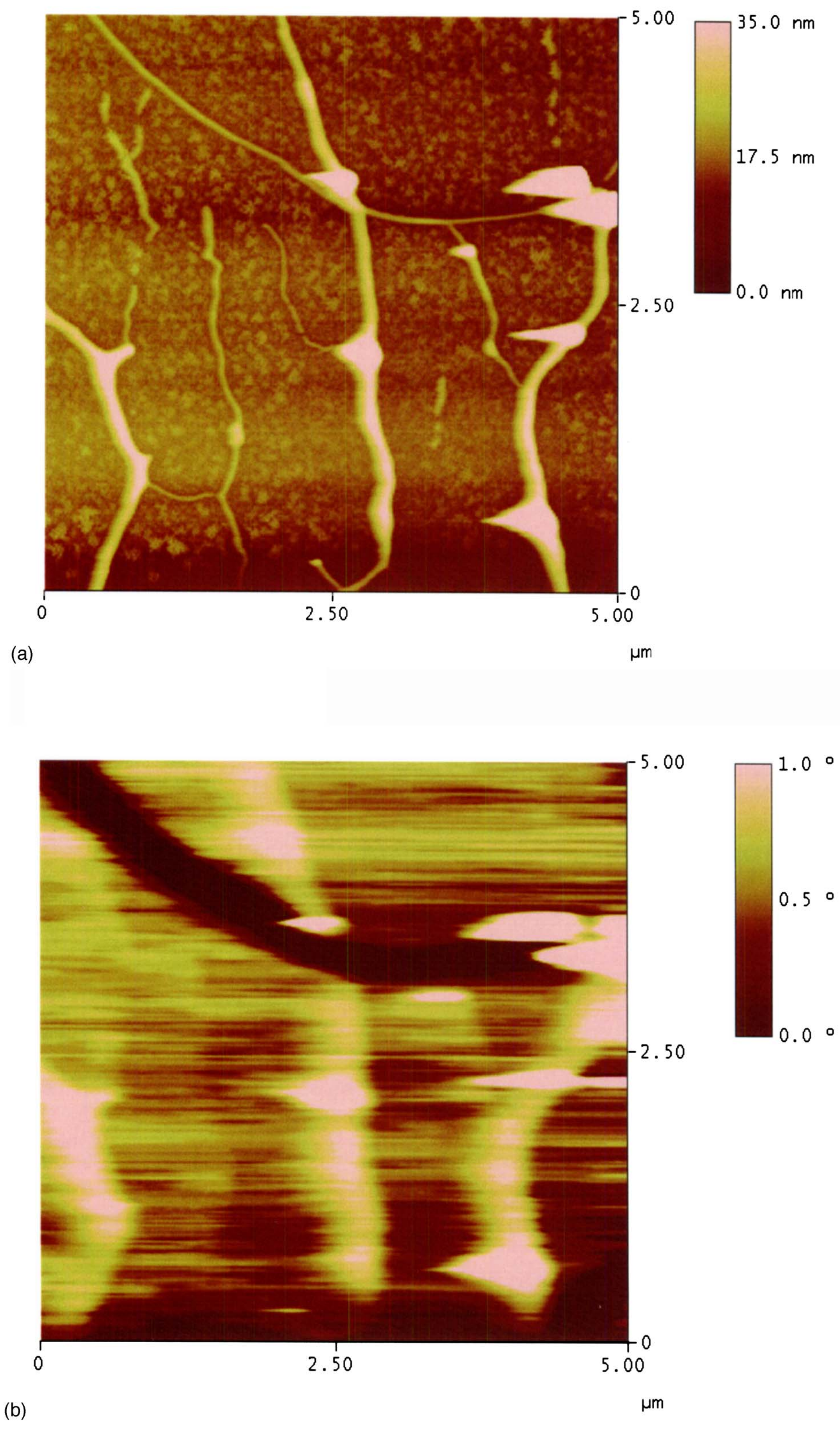

FIG. 5. (a) An AFM image of the $MOPV_4$ wires drop cast on a substrate containing carbon nanotubes. The carbon nanotube is indicated by the arrow. All other wires are $MOPV_4$. (b) An EFM image of the same region as in (a). The conducting carbon nanotube shows a clear signal in contrast to the insulating $MOPV_4$ wires.

have been observed.[14] The high breakdown voltages above 30 V also indicate that the contacts are not limiting the current. The metal electrodes are separated by 200 nm. If this gap were bridged by a conducting fiber, all the voltage would drop over the contacts in a distance of just a few nanometers. The breakdown field of the contacts would have to be on the order of $10^8$ V/cm. This is an unphysically high breakdown field. A more typical breakdown field is $10^6$ V/cm, which is on the order of the breakdown field that is obtained when one assumes that the fiber is not conducting and the voltage drops uniformly over the 200 nm gap.

To further investigate the conductivity of the wires, electrostatic force microscopy measurements were performed. In these measurements, 12 V is applied to a conducting tip that is scanned 30 nm above the sample and a scanning capacitance measurement is performed. This is a contactless measurement that can detect the presence of a conducting wire even if it is coated by an insulator. As a control, the EFM measurements were performed on a substrate that had carbon nanotubes lying on it among the $MOPV_4$ wires. The nanotubes are known to be good conductors and show a clear signal in EFM measurements. The results of these measurements are shown in Fig. 5. Figure 5(a) shows the height scan of the wires and Fig. 5(b) is the scanned conductance image. One carbon nanotube can be seen running horizontally through the image. The carbon nanotube gives a strong signal in the conductance scan. The EFM signal of the $MOPV_4$ wires is lower than that of the substrate in the measurement. This could be due to the lower dielectric constant of the wires than that of the $SiO_2$ substrate. Another contactless measurement technique is the time-resolved microwave conductivity (TRMC) measurement. Using this technique, the microwave conductivity of $MOPV_4$ wires in solution was measured. The measurements showed that the $MOPV_4$ wires had a lower conductivity than the solvent *n*-hexane. Thus no measurable conductivity could be detected.[15] Further we attempted to perform scanning potential measurements with an AFM in contact mode. This would allow us to measure over lengths shorter than 200 nm. Unfortunately, the wires were not strong enough to allow us to perform this measurement. Good conducting wires tend to be strong so this is more evidence for the poor conductivity of the wires.

## IV. DISCUSSION

Using self-assembled wires for electronic applications is appealing because the structures can be tailored at the molecular level. However, it is proving difficult to find wires that are structurally well defined and are able to carry significant currents. Our experiments cannot distinguish defects being responsible for the poor conductivity or that the wires we have studied are intrinsically poor conductors. If defects along the wires are limiting the conductivity then the average distance between the defects must be less than 200 nm, otherwise we would have sometimes measured on defect-free wires. Although the EFM probes the conductivity locally, it is not possible to measure conducting wires shorter than about 400 nm with this technique.[8] The EFM measurements confirm that there are no conducting sections of the wires longer than 400 nm. Polarized fluorescence microscopy measurements of wires deposited on a substrate indicate that there are defects in these drop cast wires and only about 70% of the dimers that form the helices are oriented perpendicular to the axis of the fiber.[1] The misorientation of the other dimers is probably due to molecule-surface interactions, fiber bending, or branching. In addition, recent calculations support the view that these wires are intrinsically poor conductors.[15] The calculations suggest that the mobility could be increased significantly if the twist angle between neighboring oligomers could be reduced.

## V. CONCLUSIONS

In conclusion, electrical transport measurements were performed on closely spaced electrodes covered with self-assembled wires of $MOPV_4$, $OPVT_4$, and bishydroxy $OPV_3$. The measurements show that the wires, as we prepared them, are poor electrical conductors. The close spacing of the electrodes allowed individual wires to bridge the electrodes and excluded the possibility that the conductivity was limited by interwire transport. Subsequent measurements indicated that the low conductivity did not arise from poor contacts. Either these wires are intrinsically poor conductors or there are defects along the wires spaced more closely than 200 nm that destroy the conductivity. Understanding why such wires are poor conductors is an important prerequisite for fabricating electronic devices using supramolecular chemistry.

## ACKNOWLEDGMENTS

We would like to thank Dr. Jing Kong for providing us with the carbon nanotube sample and Dr. Silvano De Franceschi for assistance with the EFM measurements.

[1] P. Jonkheijm, Ph.D. thesis, Eindhoven University of Technology, 2005.
[2] J. W. Hofstraat, E. W. Meijer, A. P. H. J. Schenning, and F. J. M. Hoeben, The Netherlands PCT International Application No. PCT/IB2004/050840 (23 December 2004).
[3] A. El-ghayoury, A. P. H. J. Schenning, P. A. v. Hal, J. K. J. v. Duren, R. A. J. Janssen, and E. W. Meijer, Angew. Chem., Int. Ed. **40**, 3660 (2001).
[4] M. van der Auweraer and F. C. De Schryver, Nat. Mater. **3**, 507 (2004); G. Malliaras R. Friend, Phys. Today **58**, 53 (2005).
[5] Y. Martin, D. W. Abraham, and H. K. Wickramasinghe, Appl. Phys. Lett. **52**, 1103 (1988).
[6] C. Schönenberger, and S. F. Alvaro, Phys. Rev. Lett. **65**, 3162 (1990).
[7] J. E. Stern, B. D. Terris, H. J. Mamin, and D. Rugar, Appl. Phys. Lett. **53**, 2717 (1988).
[8] M. Bockrath, N. Markovich, A. Shepard, M. Tinkham, L. Gurevich, L. P. Kouwenhoven, M. W. Wu, and L. L. Sohn, Nano Lett. **2**, 187 (2002).
[9] A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, and E. W. Meijer, J. Am. Chem. Soc. **123**, 409 (2001).
[10] P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. van Herrikhuyzen, A. P. H. J. Schenning, and E. W. Meijer, J. Am. Chem. Soc. **125**, 15941 (2003).
[11] P. Jonkheijm,A. Miura, M. Zdanowska, F. J. M. Hoeben, S. De Feyter,A. P.H.J. Schenning,F. C. De Schryver, and E. W. Meijer, Angew. Chem., Int. Ed. **43**, 74 (2004).
[12] A. Ajayaghosh and S. J. George, J. Am. Chem. Soc. **123**, 5148 (2001).
[13] A. Ajayaghosh, S. J. George, and V. K. Praveen, Angew. Chem., Int. Ed. **42**, 332 (2003).
[14] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, and C. D. Frisbie, Adv. Mater. (Weinheim, Ger.) **15**, 1881 (2003).
[15] P. Prins, K. Senthilkumar, F. C. Grozema, P. Jonkheijm, A. P. H. J. Schenning, and L. D. A. Siebbeles, J. Phys. Chem. B **109**, 18267 (2005).