CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200601320

Synthesis, Manipulation and Conductivity of Supramolecular Polymer Nanowires

Liqin Dong,[a] Tom Hollis,[b] Steven Fishwick,[b] Bernard A. Connolly,[c] Nicholas G. Wright,[b] Benjamin R. Horrocks,[a] and Andrew Houlton*[a]

Abstract: The synthesis of supramolecular conducting nanowires can be achieved by using DNA and pyrrole. Oxidation of pyrrole in DNA-containing solutions yields a material that contains both the cationic polypyrrole (PPy) and the anionic DNA polymers. Intimate interaction of the two polymer chains in the self-assembled nanowires is indicated by FTIR spectroscopy. AFM imaging shows individual nanowires to be continuous, ≈5 nm high and conformationally flexible. This feature allows them to be aligned by molecular combing in a similar manner to bare DNA and provides a convenient method for fabricating a simple electrical device by stretching DNA/PPy strands across an electrode gap. Current–voltage measurements confirm that the nanowires are conducting, with values typical for a polypyrrole-based material. In contrast to polymerisation of pyrrole on a DNA template in bulk solution, attempts to form similar wires by polymerisation at surface-immobilised DNA do not give a continuous coverage; instead, a beads-on-a-string appearance is observed suggesting that immobilisation inhibits the assembly process.

Keywords: conducting materials · DNA · nanowires · polymers · self-assembly

Introduction

Considerable recent efforts have focused on the self-assembly of molecular building blocks as a means of realising nanometer-scale electronic components and devices.[1] Biopolymers, and DNA in particular, are well suited to building systems and architectures spanning the nm–μm length scale;[2,3] however, the intrinsically low conductance of this material[4] necessitates further functionalisation for electronic applications. This can be overcome by templating[5] and the deposition of metals such as Cu,[6,7] Ag,[8,9] Au[10,11] and Pd[12] or MoGe alloy,[13] single-wall carbon nanotubes[14,15] and nanoparticles,[16] have been demonstrated as methods for preparing conducting nanowire systems.

Conducting polymers are attractive materials for nanoscale electronics[17] as well as for chemical and biological sensors, due to their ease of synthesis and stability. The ability to tune their conductivity by molecular design may offer new fabrication strategies and applications. Although the interaction of cationic conducting polymers with DNA is known and has been exploited previously for bioanalytic applications,[18] there have been surprisingly few attempts to combine these materials for nanometer-scale electronics.[19–21]

We have demonstrated previously the synthesis and immobilisation of bulk polypyrrole (PPy) films at DNA-modified silicon electrodes.[22] The immobilisation arises from electrostatic interaction between the cationic, oxidised PPy and the polyanionic DNA. We reasoned that, because pyrrole oligomers formed during the initial stages of oxidative polymerisation exhibit DNA-binding motifs, the formation of individual DNA:PPy hybrid strands should also be possible through supramolecular interactions (Scheme 1).

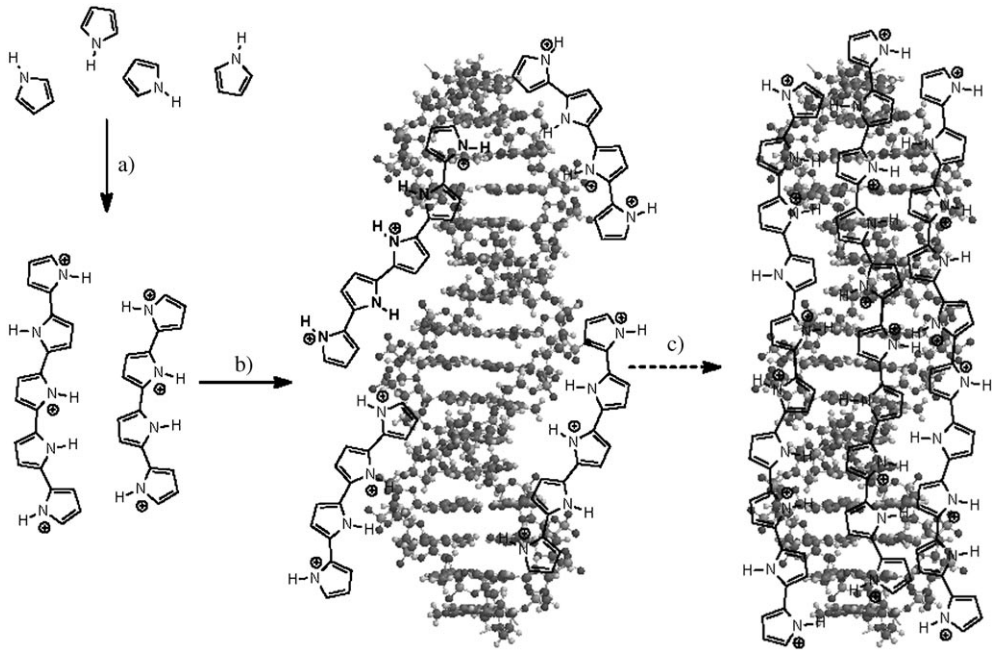
Here, we report on the synthesis of individual supramolecular nanowires based on DNA-templating of PPy. The syntheses were performed in solution and at surface-immobilised DNA, and the resulting materials were characterised

[a] Dr. L. Dong, Dr. B. R. Horrocks, Prof. A. Houlton
Chemical Nanoscience Laboratories, School of Natural Sciences
University of Newcastle, Newcastle upon Tyne, NE1 7RU (UK)
Fax: (+44) 191-222-6929
E-mail: andrew.houlton@ncl.ac.uk

[b] T. Hollis, S. Fishwick, Prof. N. G. Wright
School of Electrical, Electronic and Computing Engineering
University of Newcastle, Newcastle upon Tyne, NE1 7RU (UK)

[c] Prof. B. A. Connolly
Institute of Cell and Molecular Biosciences
University of Newcastle, Newcastle upon Tyne, NE2 4HH (UK)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.



Scheme 1. Proposed mechanism of self-assembly of DNA/PPy nanowires. a) Oxidation of pyrrole monomer with $FeCl_3$, b) association of oligomers on DNA through supramolecular interactions, c) polymer growth on DNA template.

by IR spectroscopy, AFM and two-terminal *I–V* measurements.

Results and Discussion

Polymerisation of pyrrole in DNA-containing solutions: A common method for preparing polypyrrole (PPy) involves chemical oxidation of the pyrrole monomer in organic or aqueous solution.[17] $FeCl_3$ is a typical oxidant and this was used here for DNA-templated reactions. Firstly, the effect of incubating supercoiled plasmid DNA with $FeCl_3$ was investigated to establish whether strand cleavage would be problematic at the concentrations and reaction times employed. The use of supercoiled DNA provides a stringent test of strand cleavage because even single-strand breaks are readily observed due to the markedly different mobility of supercoiled and relaxed forms. Some evidence for single-strand cuts was observed, but only after reaction times longer than those in the polymerisation experiments. More significantly, there was no evidence of linear DNA, indicating that, although some single-strand nicks may occur, these are at a sufficiently low frequency to make strand scission negligible during the formation of DNA–polypyrrole nanowires (DNA/PPy).

The synthesis of DNA/PPy nanowires involved addition of an aqueous pyrrole solution to a solution of DNA. A solution of $FeCl_3$ was immediately added to start the polymerisation. FTIR spectra of the isolated material provided evidence of the formation of a supramolecular hybrid polymer containing DNA and polypyrrole (Figure 1) (see also Figure S1 and Table S1 in the Supporting Information). One of

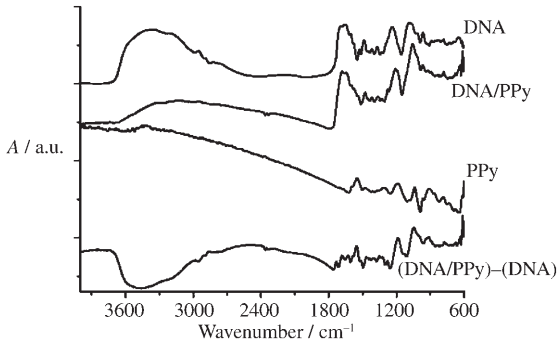


Figure 1. FTIR spectra of DNA/PPy complex vs. controls. Infrared spectra of DNA, DNA/PPy complex, PPy and the difference spectrum (DNA/PPY)−(DNA) are shown.

the significant features indicating the incorporation of *conducting* polypyrrole in the hybrid polymer is the appearance of a broad absorption above 2000 cm^{-1}: this is well known to be due to intrachain (free carrier) excitations.[23] The sample of pure polypyrrole prepared in the absence of DNA exhibits a similar broad absorption band in this region. However, in DNA itself, no such broad absorption above 2000 cm^{-1} was observed, instead a large band centred at $\approx$3300 cm^{-1} due to bound water and N−H is observed. This feature is also partly observed in the DNA/PPy (decrease in absorbance at $>$3300 cm^{-1}), as well as the strong feature just below 1800 cm^{-1}. The presence of DNA in the DNA/PPy is revealed clearly in the 1100 to 1800 cm^{-1} region (Figure 1 and Figure S1), and the spectra of both DNA itself and the hybrid polymer are similar in this region, though some peak shifts are observed. Polypyrrole itself exhibits ab-

sorptions significantly different from both DNA and the hybrid polymer in this region, especially the broad absorption at 900 cm^{-1}. This feature is not immediately apparent in the DNA/PPy spectrum because of the intense DNA bands just above 1000 cm^{-1}, however, the difference spectrum obtained directly by subtracting the DNA spectrum shown from that of the DNA/PPy shows clearly the characteristic 900 cm^{-1} band of the PPy in the nanowires.

The IR spectra also show that the DNA/PPy sample is not a simple mixture of DNA and PPY, but rather indicate an intimate interaction of DNA with PPy in the hybrid polymer (Figure S1 and Table S1). The negative feature in the difference spectrum at 3300 cm^{-1} shows that bound water has been displaced from the polymer. A careful examination of the fingerprint region reveals that the DNA-related bands are slightly shifted relative to the pure DNA spectrum. In DNA itself, vibrations associated with the PO_2^- symmetric stretching at 1086 cm^{-1}, along with P–O or C–O backbone stretching at 1070 cm^{-1}, as well as with C–O deoxyribose stretching at 1022 cm^{-1}, are observed as a broad, slightly split band. In the DNA/PPy, the splitting is lost and the band is shifted to lower energy (1057 cm^{-1}). Furthermore, PPy itself has a vibration at 1039 cm^{-1}. The PO_2^- asymmetric stretching vibration (1238 cm^{-1} in the free DNA) is also shifted to lower frequency in the hybrid material (1207 cm^{-1}), and a small peak at 1277 cm^{-1} appears in the hybrid material, although PPy itself has a vibration at lower frequency (1187 cm^{-1}) attributed to a pyrrole-ring breathing mode. Moreover, in DNA, the vibrations associated with the nucleobases at 1371, 1485, 1657 and 1690 cm^{-1} are all shifted to lower frequencies in the hybrid material (see Supporting Information). One exception is the mode at 1530 cm^{-1} due to the in-plane vibration of cytosine and guanine, which is shifted to higher energies (1539 cm^{-1}) in DNA/PPy. Because we observe all the bands of PPy in the difference spectrum (though some are shifted with respect to pure PPy: Figure S1 and Table S1), these spectral changes suggest that interactions of the PPy with the DNA strands involve both the phosphate/phosphodiester backbone and the nucleobases.

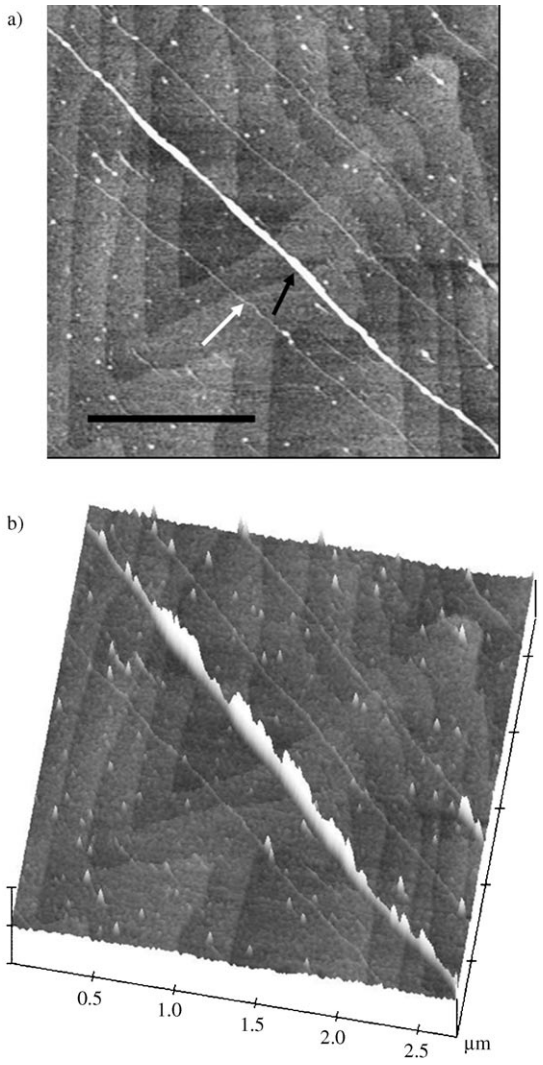


Figure 2. DNA/PPy stretched on alkylated silicon (111) surfaces. a) AFM image showing that material isolated from the reaction contains bare DNA-scaffold molecules (white arrow) and thicker DNA/PPy nanowire (black arrow). The coverage of the DNA/PPy strand is seen to be highly continuous. Scale bar = 1 μm, height scale is 4 nm. b) Surface plot highlighting the height variation along a single DNA/PPy nanowire (black arrow in (a)), which ranges from 2.6–6.6 nm. Height scale is 7 nm.

Stretching and alignment of DNA/PPy strands: When the DNA/PPy strands formed in solution were deposited on mica and studied by using non-contact AFM (Figure S2), the strands appeared to be randomly coiled on the surface. Thickening of some of the strands relative to the dimensions of bare DNA alone is clearly evident (≈3–6 nm). There are also large globular particulates (height ≈ 16 nm), which are probably non-templated polypyrrole. However, on hydrophobic surfaces, such as an alkylated silicon (111) wafer,[24] it was possible to stretch the DNA/PPy by *molecular combing* to create highly aligned isolated strands (Figure 2) in a similar manner to native DNA.[25,26] This is possible because the interaction between the hydrophilic DNA/PPy and the hydrophobic surface is much weaker than between DNA/PPy and mica. That the DNA/PPy strands retain the ability to be combed, because of their conformational flexibility, proved to be especially useful for manipulation during the fabrication of a simple electrode device (see below). Figure 2 shows individual DNA/PPy strands to have a highly continuous coverage over several microns. Differences are evident in the width and height along the length of individual strands (Figure 2b), with heights ranging from around 2.6 to 6.6 nm (average of around 5 nm) and widths ranging from 30 to 63 nm (average of around 48 nm). Also evident in the images are much thinner strands; the height and the width of these are almost constant, with heights ranging from 0.7 to 1.3 nm. These values are entirely consistent with other studies of single duplex DNA molecules by AFM[26] and indicate that not all of the template DNA is modified during reaction.

These data further support the FTIR data and indicate that polyanionic DNA molecules are a suitable template for directing the growth of polycationic polypyrrole nanowires. The differences in the increased height/width at different continuous sections of particular single wires compared to bare DNA identify the assembly of PPy on the DNA molecule. The resulting material can be considered a supramolecular polymer assembly of DNA and PPy. AFM analysis of material isolated from control experiments performed in the absence of pyrrole (i.e., DNA and $FeCl_3$) gave, as expected, strands that extended over several microns with metrics characteristic of bare duplex DNA molecules.

Attempts to polymerise pyrrole at surface-immobilised DNA, again by using $FeCl_3$ as oxidant, produced strands with a rather different appearance to those from solution-phase reactions. AFM showed these strands to have a *beads-on-a-string* appearance, with particulate PPy bound along the length of the DNA (Figure 3). Section analysis indicates

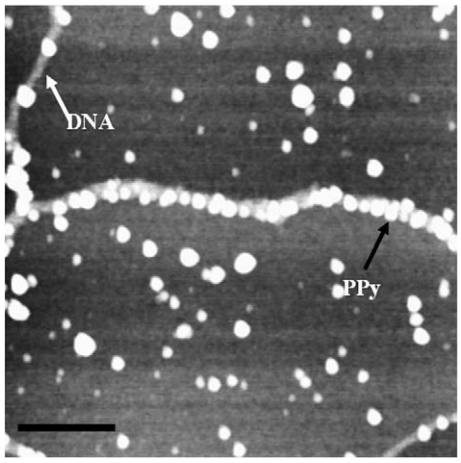


Figure 3. AFM image of immobilised DNA on mica after in situ polymerisation of pyrrole. Non-specific absorption of polymer particulates is evident as bright spots. Scale bar = 200 nm, height scale is 4 nm.

that these features have increased height and width, ≈6 and 36 nm, respectively, relative to free DNA (height ≈1 nm, width ≈14 nm). In these samples, non-specific absorption of polymer particulates to the surface is also more evident, though the majority of the polypyrrole appears to be associated with DNA.

Although mica-immobilised DNA can act as a template for PPy, the *beads-on-a-string* appearance suggests that although nucleation occurs at numerous points along the DNA backbone, polymer growth does not proceed continuously along the strand. Furthermore, handling and analysis lead to loss of the beads from the DNA strands. This suggests that the fine details of the DNA–polypyrrole interactions of material assembled on mica surfaces are different to those produced in solution. In both cases, polymer growth is likely to be initiated at many points along the DNA, and the lower dimensional freedom of surface-immobilised strands appears to inhibit strand growth. In free solution, nucleation and strand extension may be followed by increased supramolecular interactions, possibly including interwinding of PPy and DNA strands, accounting for the increased robustness of the resulting material.

Alignment and electrical conductivity of PPy nanowires: To measure the conductivity of the DNA-templated nanowires, the current–voltage (*I–V*) characteristics were investigated by using a simple two-terminal electric circuit. This was fabricated by positioning DNA/PPy strands formed in solution (or bare DNA as controls) across the gap between two gold electrodes. The oxide between the gold electrodes was treated with chlorotrimethylsilane (Me_3SiCl) to produce a hydrophobic surface suitable for stretching and aligning the DNA/PPy nanowires. AFM imaging confirmed that, after combing an aqueous drop containing preformed DNA/PPy, one or more nanowires spanned the electrodes. Figure 4 shows an AFM image of part of the actual electrical-measurement device incorporating one single bridging DNA/PPy nanowire (Figure S5). The DNA/PPy nanowire shows continuous growth and variation in diameter, as described above.

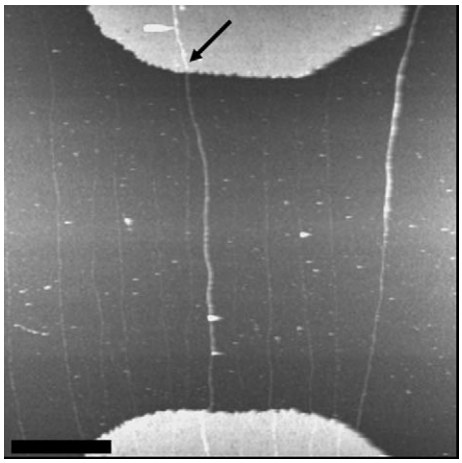


Figure 4. AFM image of part of the actual electrical-measurement device fabricated to measure the electrical conductivity of the DNA/PPy nanowires. The image shows one DNA/PPy nanowire (black arrow) with diameter ≈5.2 nm and length ≈7 μm, bridging the gap in the device. Scale bar = 2 μm.

A two-terminal *I–V* measurement was performed on this device and confirmed charge transport involving the DNA/PPy nanowires. The *I–V* measurements exhibit a reproducible, non-linear response (Figure 5) at room temperature, typical of the formation of Schottky barriers at the PPy nanowire/gold electrode interfaces.[27,28] This phenomenon has been observed for other systems such as polyaniline-based nanofibres[29] and Au-PPy-Au nanorods.[30]

The resistance obtained from the linear portion of the graph (inset Figure 5) is around 843 MΩ. This resistance, as in all two-terminal measurements of nanowires, will include a contribution from the barriers at the wire/Au interface and, therefore, represents an upper boundary to the resist-

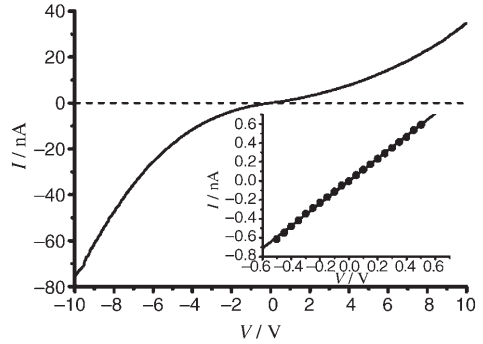


Figure 5. Current–voltage (*I–V*) measurements for the device with one DNA/PPy nanowire (solid line) bridging the gap shown at the top of the image in Figure 4. In contrast, insulating behaviour (dashed line) is demonstrated between electrode and oxide. Inset: the ohmic region at small bias voltage corresponds to a resistance of 843 MΩ. Note: the *I–V* curve obtained with DNA molecules bridging the gap in the absence of polypyrrole gave a measured resistance $>10^{14}$ Ω, confirming that DNA of this length is insulating. This is in line with the results of others (Figure S6).

ance of the nanowire itself. Nevertheless, by using the topography from AFM, we can make a comparison with the conductivity of polypyrrole obtained by other procedures. Assuming the DNA/PPy wire bridging the gap in the device has a length of ≈7 μm and a diameter of ≈5.2 nm, this gives an approximate room-temperature conductivity of ≈4 $S\,cm^{-1}$ (lower boundary). This conductivity is of the same order as the conductivity of bulk polypyrrole powder (1.7 $S\,cm^{-1}$) prepared chemically by using $FeCl_3$ as oxidant.[23] Moreover, the room-temperature conductivity of DNA/PPy nanowires fabricated on DNA templates is markedly higher (≈10^3) than the previously reported rod-shaped PPy scaffolded by alumina templates (≈3 $mS\,cm^{-1}$).[30] The above observations, in combination with all of the control measurements (no detectable current for bare DNA, see Supporting Information), demonstrate that the electric current detected is carried solely by the PPy nanowires scaffolded by DNA templates.

Discussion

DNA-templated conducting metal wires, prepared by solution-phase methods, have been known for some time. These metallic wires are typically 30–100 nm thick, depending on preparation route, and tend to have a continuous, though granular or dendritic, appearance. Very recently, highly homogeneous, ultrathin (5–15 nm) nanowires of superconducting $Mo_{21}Ge_{79}$ have been fabricated by the metallisation of DNA by sputtering.[13]

By comparison, DNA-templated nanowires derived from conducting organic polymers, and based on polyaniline, have emerged only recently.[21,31] Enzymatic polymerisation (horse radish peroxidase/H_2O_2 at pH 4) of aniline at silica-immobilised DNA has been reported,[31] as well as a range of polymerisation methods in solution, including horse radish peroxidase/H_2O_2, $[Ru(bipy)_3]^{2+}$ and $(NH_4)_2S_2O_8$ at pH 3–5. In all of these cases, AFM imaging shows strands with somewhat incomplete coverage of the DNA and the formation of polymer domains or particles. The low pH required for protonation of polyaniline, necessary to effect electrostatic binding to DNA, is clearly a concern if using DNA as a template, as it is sensitive to acid-cataysed depurination. This may be a factor in the non-continuous growth observed, another appears to be surface immobilisation. To date, polymerisation reactions at surface-immobilised DNA, for polyaniline[21,31] and polypyrrole (this study), have resulted in strands with this type of appearance. In contrast, DNA/PPy wires prepared in solution show continuous coverage and are smooth compared to typical metal-based wires.

In addition to DNA templating, considerable efforts have focused on the preparation of conducting polymer nanowires (or other one-dimensional nanostructures, especially nanotubes and nanorods) by alternative methods. For bulk preparations, templating in porous inorganic solids such as alumina,[30,32] zeolites,[33] or polymer membranes[34] has been developed, and more recently, seeding[33,35,36] and surfactant doping have been used.[37,38] For individually isolated wires, electrochemical deposition in fabricated structures such as channels[39] or electrode gaps[19,20,40] has produced wires with widths ranging from 100 nm[40] to <20 nm.[20] Direct writing with an Electrochemical Dip-Pen method has been used to prepare wires of ≈30 nm.[41] In contrast to these approaches, the DNA-templating method gives conducting wires whose widths are amongst the smallest for chemically prepared nanowires.[42]

Conclusion

The present results demonstrate the directed assembly of conducting polymer nanowires on DNA as a template. Differences in the resulting supramolecular strands are apparent for reactions carried out on surface-immobilised DNA and DNA free in solution. The former method results in a *beads-on-a-string* appearance for the strands; in contrast, nanowires prepared in solution have coverage of DNA that is essentially smooth and continuous. The latter type of strand is electrically conducting and conformationally flexible, allowing alignment of the polymer nanowires by molecular combing in the same manner as DNA itself. To our knowledge, similar flexibility for other types of DNA-templated material has not been demonstrated. This facilitates the positioning of the nanowires at electrode junctions, and may offer a convenient method to fabricate more-complex arrangements, such as one- and two-dimensional arrays.

Experimental Section

DNA-templated synthesis of polypyrrole in solution: An aqueous solution of pyrrole (5 μL, 1 mM) was added to 100 μL of λ-DNA solution (100 $ng\,\mu L^{-1}$ diluted in Nanopure water, containing 0.5 mM $MgCl_2$), and

the solution was mixed thoroughly. Aqueous $FeCl_3$ (5 μL, 1 mM) as oxidant was added. The solution was mixed and incubated for 1 h at RT. The resulting material was analysed by AFM by placing ≈10 μL of the reaction mixture onto the appropriate support (either mica or alkylated Si(111) surface).

DNA-templated synthesis of polypyrrole at surface-immobilised DNA: A 10-μL drop of λ-DNA solution containing 0.5 mM $MgCl_2$ was deposited onto a freshly cleaved mica and left to adsorb for 5 min. The surface was rinsed with Nanopure water and blown dry by using compressed air. Immediately following DNA deposition, freshly distilled pyrrole (≈2 μL) was allowed to incubate with the DNA for 10 s. After removing the pyrrole by using compressed air, the surface was spotted with 10 μL of a 0.1-M $FeCl_3$ solution and allowed to react for 10 s. The surface was then rinsed thoroughly with water, dried with compressed air and characterised by AFM. Control experiments in which DNA was treated with either pyrrole or $FeCl_3$ alone showed no change by AFM.

Alignment and stretching of DNA/PPy strands: Alkylated Si(111) substrates were prepared as described previously by using 4,4,-dimethoxytrityl-undecenol.[24] These surfaces are hydrophobic and atomically flat and proved well suited for aligning native and polymer-functionalised DNA by molecular combing.[25,26] Typically, a 10-μL drop of the λ-DNA/PPy reaction mixture was pipetted onto the alkylated Si surface. The droplet was then dragged by using a pipette to pull the solution across the surface in one direction. The surface tension at the moving air/water interface is sufficient to stretch the molecules in the direction of movement.

Infrared spectroscopy: Spectra (in the range 600–4000 cm^{-1} with spectral resolution of 4 cm^{-1}) were obtained by using a Biorad FTS-40 spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector in normal transmission alignment. The DNA used was from Herring testes, type XIV (Sigma-Aldrich, average molecular weight ≈700 bp). A DNA concentration of ≈1 mg mL^{-1} was used in the IR spectroscopy study. All samples and controls were deposited on clean Si(111) substrate.

AFM imaging: AFM imaging was performed in air by using Tapping Mode on a Multimode Nanoscope IIIa (Veeco, Metrology group) and NanoProbe tips (Veeco). All of the AFM images shown are height images, unless otherwise indicated.

Electrical measurements of PPy nanowire devices: Conductivity measurements were performed by using gold electrodes deposited on oxidised silicon. Firstly, five pairs of small finger electrodes of e-beam evaporated metals (3 nm titanium followed by 5 nm gold) were patterned by using photolithography and wet etching, the gap between each pair of fingers ranging from none to several micrometers. Next, five pairs of large pads were patterned by using photolithographic lift-off from e-beam evaporated layers of 10 nm of titanium followed by 100 nm of gold. The two pads in each pair are separated by 100 μm. The two small gold fingers in each pair provide contacts to the DNA-templated PPy wires (or DNA molecules), and the two large gold pads in each pair serve as electrical contacts for external measurement of the system. Prior to aligning of DNA, the oxide layer was treated with $SiClMe_3$ vapour to produce a hydrophobic surface between the metal electrodes to facilitate molecular combing.

Onto these electrodes, 6 μL of an aqueous solution of PPy nanowires (or DNA (100 ng μL^{-1} λ-DNA solution containing 1 mM $MgCl_2$) as a control) was deposited and aligned across the gap between the gold fingers by using molecular combing.[25,26]

Measurements were made by using a Teledyne probing station and electrical measurements were conducted by using a HP1455A semiconductor parameter analyser on devices. For each of the electrical tests, the current was measured for applied voltages from −10 to 10 V in steps of 0.05 V. All of the electrical measurements were carried out at RT in air without light illumination.

Acknowledgements

We thank Dr Hector Figueioredo of BAE Systems, European Union FP6 and the EPSRC for financial support of this work.

[1] G. A. Ozin, A. C. Arsenault, *Nanochemistry: A Chemical Approach to Nanomaterials*, RSC, Cambridge, **2005**.
[2] a) E. Braun, K. Keren, *Adv. Phys.* **2004**, *53*, 441–496; b) N. C. Seeman, *Nature* **2003**, *421*, 427–431; c) C. M. Niemeyer, C. A. Mirkin, *NanoBiotechnology: Concepts, Methods and Applications*, Wiley-VCH, Weinheim, **2004**.
[3] a) A. P. Alivisatos, K. P. Johnsson, X. G. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez, P. G. Schultz, *Nature* **1996**, *382*, 609–611; b) C. A. Mirkin, *Inorg. Chem.* **2000**, *39*, 2258–2272.
[4] D. Porath, A. Bezryadin, S. de Vries, C. Dekker, *Nature* **2000**, *403*, 635–638.
[5] Q. Gu, C. Cheng, R. Gonela, S. Suryanarayanan, S. Anabathula, K. Dia, D. T. Haynie, *Nanotechnology* **2006**, *17*, R14–R25.
[6] C. F. Monson, A. T. Woolley, *Nano Lett.* **2003**, *3*, 359–363.
[7] H. A. Becerril, R. M. Stoltenberg, D. R. Wheeler, R. C. Davis, J. N. Harb, A. T. Woolley, *J. Am. Chem. Soc.* **2005**, *127*, 2828–2829.
[8] E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, *Nature* **1998**, *391*, 775–778.
[9] H. Yan, S. H. Park, G. Finkelstein, J. H. Reif, T. H. LaBean, *Science* **2003**, *301*, 1882–1884.
[10] F. Patolsky, W. Weizmann, O. Liobasheveski, I. Willner, *Angew. Chem.* **2002**, *114*, 2429–2433; *Angew. Chem. Int. Ed.* **2002**, *41*, 2323–2327.
[11] T. Nishinaka, A. Takano, Y. Doi, M. Hashimoto, A. Nakamura, Y. Matsushita, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.* **2005**, *127*, 8120–8125.
[12] J. Richter, M. Mertig, W. Pompe, I. Monch, H. K. Schackert, *Appl. Phys. Lett.* **2001**, *78*, 536–538.
[13] D. S. Hopkins, D. Pekker, P. M. Goldbart, A. Bezryadin, *Science* **2005**, *308*, 1762–1765.
[14] H. Xin, A. T. Woolley, *J. Am. Chem. Soc.* **2003**, *125*, 8710–8711.
[15] K. Keren, R. S. Berman, E. Buchstab, U. Sivan, E. Braun, *Science* **2003**, *302*, 1380–1382.
[16] W. U. Dittmer, F. C. Simmel, *Appl. Phys. Lett.* **2004**, *85*, 633–635.
[17] T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds in *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York, **1998**.
[18] A.-H. Bae, T. Hatano, M. Numata, M. Takeuchi, S. Shinkai, *Macromolecules* **2005**, *38*, 1609–1615.
[19] H. He, J. Zhu, N. J. Tao, L. A. Nagahara, I. Amlani, R. Tsui, *J. Am. Chem. Soc.* **2001**, *123*, 7730–7731.
[20] H. X. He, C. Z. Li, N. J. Tao, *Appl. Phys. Lett.* **2001**, *78*, 811–813.
[21] a) Y. Xiao, A. B. Kharitonov, F. Patolsky, Y. Weizman, I. Willner, *Chem. Commun.* **2003**, 1540–1541; b) P. Nickels, W. U. Dittmer, S. Beyer, J. P. Kotthaus, F. C. Simmel, *Nanotechnology* **2004**, *15*, 1524–1529.
[22] A. R. Pike, S. N. Patole, N. C. Murray, T. Ilyas, B. A. Connolly, B. R. Horrocks, A. Houlton, *Adv. Mater.* **2003**, *15*, 254–257.
[23] M. Omastova, M. Trchova, J. Kovarova, J. Stejskal, *Synth. Met.* **2003**, *138*, 447–455.
[24] S. N. Patole, A. R. Pike, B. A. Connolly, B. R. Horrocks, A. Houlton, *Langmuir* **2003**, *19*, 5457–5463.
[25] J. W. Li, C. L. Bai, C. Wang, C. F. Zhu, Z. Lin, Q. Li, E. H. Cao, *Nucleic Acids Res.* **1998**, *26*, 4785–4786.
[26] Z. X. Deng, C. D. Mao, *Nano Lett.* **2003**, *3*, 1545–1548.
[27] P. Syed Abthagir, R. Saraswathi, *J. Appl. Polym. Sci.* **2001**, *81*, 2127–2135.
[28] C. Nguyen Van, K. Potje-Kamloth, C. Nguyen Van, *J. Phys. D* **2000**, *33*, 2230–2238.
[29] Y. X. Zhou, M. Freitag, J. Hone, C. Staii, A. T. Johnson, N. J. Pinto, A. G. MacDiarmid, *Appl. Phys. Lett.* **2003**, *83*, 3800–3802.
[30] S. Park, S.-W. Chung, C. A. Mirkin, *J. Am. Chem. Soc.* **2004**, *126*, 11772—11773.
[31] Y. Ma, J. Zhang, G. Zhang, H. He, *J. Am. Chem. Soc.* **2004**, *126*, 7097–7101.
[32] M. G. Han, S. H. Foulger, *Chem. Commun.* **2005**, 3092–3094.
[33] M. Ikegame, K. Tajima, T. Aida, *Angew. Chem.* **2003**, *115*, 2204–2207; *Angew. Chem. Int. Ed.* **2003**, *42*, 2154–2157.
[34] C. R. Martin, *Acc. Chem. Res.* **1995**, *28*, 61–68.

[35] X. Zhang, W. J. Goux, S. K. Manohar, *J. Am. Chem. Soc.* **2004**, *126*, 4502–4503.
[36] X. Zhang, S. K. Manohar, *J. Am. Chem. Soc.* **2004**, *126*, 12714–12715.
[37] C. He, C. Yang, Y. Li, *Synth. Met.* **2003**, *139*, 539–545.
[38] T. Hatano, A.-H. Bae, M. Takeuchi, N. Fujita, K. Kaneko, H. Ihara, M. Takafuji, S. Shinkai, *Angew. Chem.* **2004**, *116*, 471–475; *Angew. Chem. Int. Ed.* **2004**, *43*, 465–469.
[39] R. M. Hernandez, L. Richter, S. Semancik, S. Stranick, T. E. Mallouk, *Chem. Mater.* **2004**, *16*, 3431–3438.
[40] K. Ramanathan, M. Bangar, M. Yun, W. Chen, M. V. Myung, A. Mulchandani, *J. Am. Chem. Soc.* **2005**, *127*, 496–497.
[41] B. W. Maynor, S. F. Filocamo, M. W. Grinstaff, J. Liu, *J. Am. Chem. Soc.* **2002**, *124*, 522–523.
[42] Footnote: A meaningful comparison of conductance values for different preparation methods is non-trivial due to a lack of data on doping levels.

Received: September 14, 2006
Published online: December 11, 2006

