Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Chemical and electrochemical routes to rhodium nanowires using DNA-templating.

Supporting Information.

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Fourier Transform Infra-Red (FTIR) spectroscopy of the DNA/Rh^{+3} system

For FTIR studies, samples were prepared as films of material upon silicon substrates. Samples for DNA/Rh^{3+} were prepared by mixing an aqueous solution of CT-DNA (30 µL; 500 µg mL^{-1}) with an aqueous solution of $RhCl_3.xH_2O$ (30 µL; 2.5 mM). The resulting DNA/Rh^{3+} solution were allowed to stand at room temperature for 20 minutes. Then 80 µL of the reaction solution was deposited upon a silicon substrate, and the solvent was allowed to evaporate at room temperature. Samples of bare DNA were prepared in a similar manner. FTIR spectra were performed with a Bio-Rad Excalibur FTS-40 spectrometer (Varian Inc., Palo Alto, CA, USA), and spectra were recorded over the 400–4000 cm^{-1} range, with 128 scans and at 4 cm^{-1} resolution.

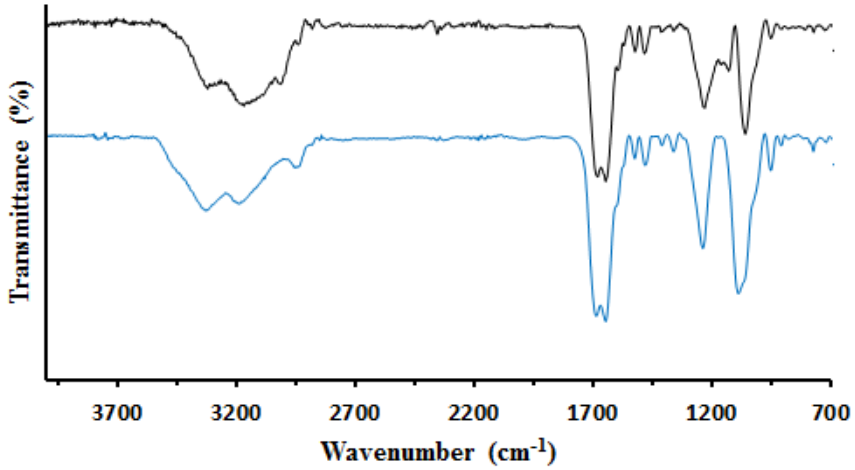


Figure S1(a): FTIR data of calf thymus DNA (lower, blue spectrum) vs DNA/Rh^{3+} system (upper, black spectrum) in the 700-4000 cm^{-1} region.

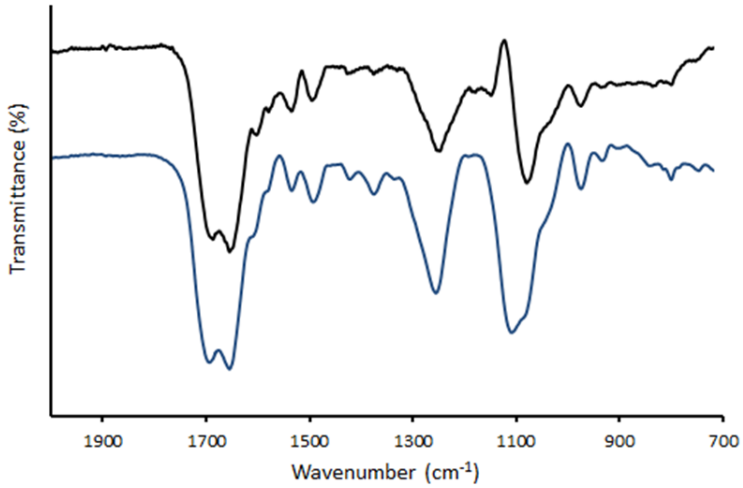


Figure S1(b): FTIR data of calf thymus DNA (lower, blue spectrum) vs DNA/Rh^{3+} system (upper, black spectrum) in the 700-2000 cm^{-1} region.

Wavenumber (cm^{-1})		Assignment
CT-DNA	**CT-DNA/ Rh^{3+}**	
960	960	C-C deoxyribose stretch
1033[a]	1019 [a]	C-C deoxyribose stretch
1071	1068	P-O/C-O deoxyribose stretch
1097	-	PO_2^- symmetric stretch
-	1137	PO_2^- asymmetric stretch
1246	1238	PO_2^- asymmetric stretch
1368	1367	C-N stretch of cytosine / guanine
1416	1417	C-H / N-H deformation; C-N stretch
1488	1490	Ring vibration of cytosine / guanine
1529	1530	In-plane vibration of guanine / cytosine
1603	1600	In-plane vibration of adenine
1653	1653	C=O stretch of cytosine / thymine; In-plane vibration of thymine
1692	1688	C=O stretch of guanine / thymine; N-H thymine
2850–3500	2850–3500	C-H / N-H / O-H stretches

Table S1. Assignment and comparison of FTIR spectra (700–4000 cm^{-1}) of calf thymus DNA, and calf thymus DNA following association of with Rh^{3+} cations in aqueous solution. [a]Peak appeared as a shoulder.[1-3] Comparison of the spectra indicate that the binding of the Rh^{3+} ions/species takes place both at the nucleobases and phosphodiester backbone of the DNA. This is evident from changes in position and intensity of DNA-related bands, seen especially in the 900–1300cm^{-1} region of the spectra. Of particular note is the band at 1246cm^{-1} in the spectrum of DNA, attributed asymmetric PO_2^- vibrations in the backbone, shifts to lower wavenumber (1238cm^{-1}) following metal association. Differences are also

noted in the 1300–1800cm^{-1} region of the spectra, in which several of the bands correspond to vibrations associated with the nucleobases, can be identified. For example, the N-H deformation centred at 1416cm^{-1} and the C-N stretch band from guanine/cytosine observed at 1368cm^{-1} are seen to be reduced in intensity in the DNA/Rh^{3+} spectrum, whilst the carbonyl stretch at 1692cm^{-1} in DNA spectrum shifts to lower wavenumber (1688cm^{-1}) after treatment with metal salt.

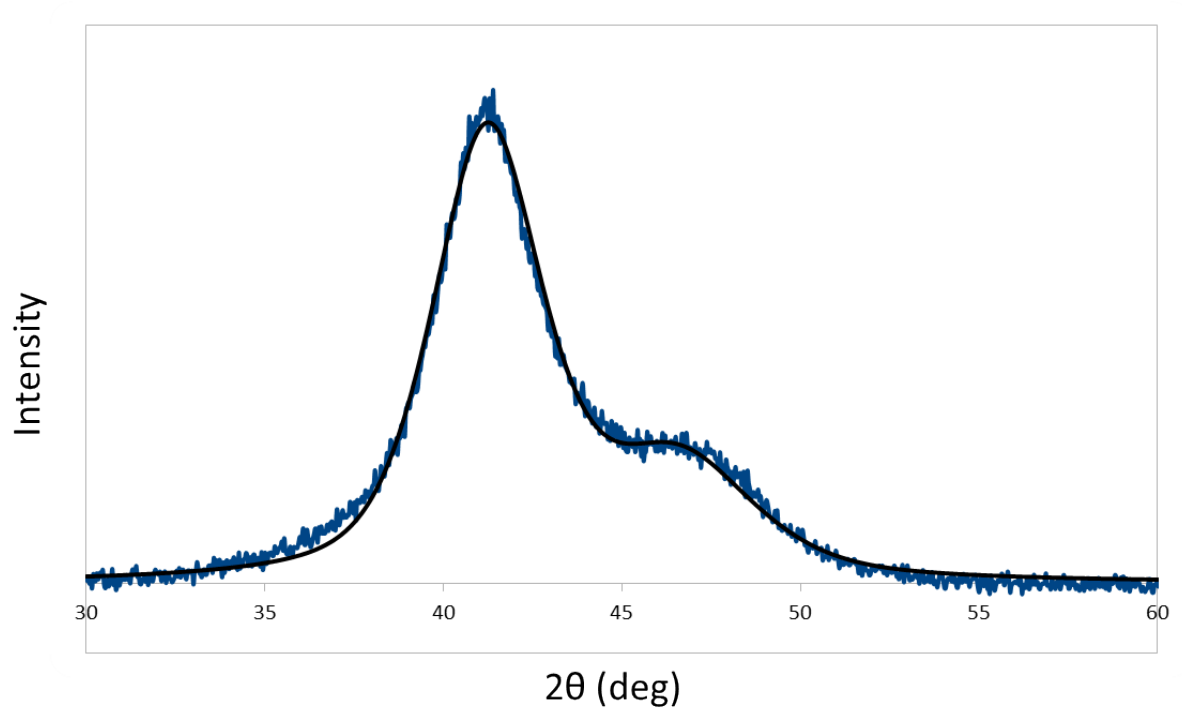


Figure S2. Powder XRD data for Rh/DNA_{Chem} nanowires fitted to two pseudo Voigt functions.

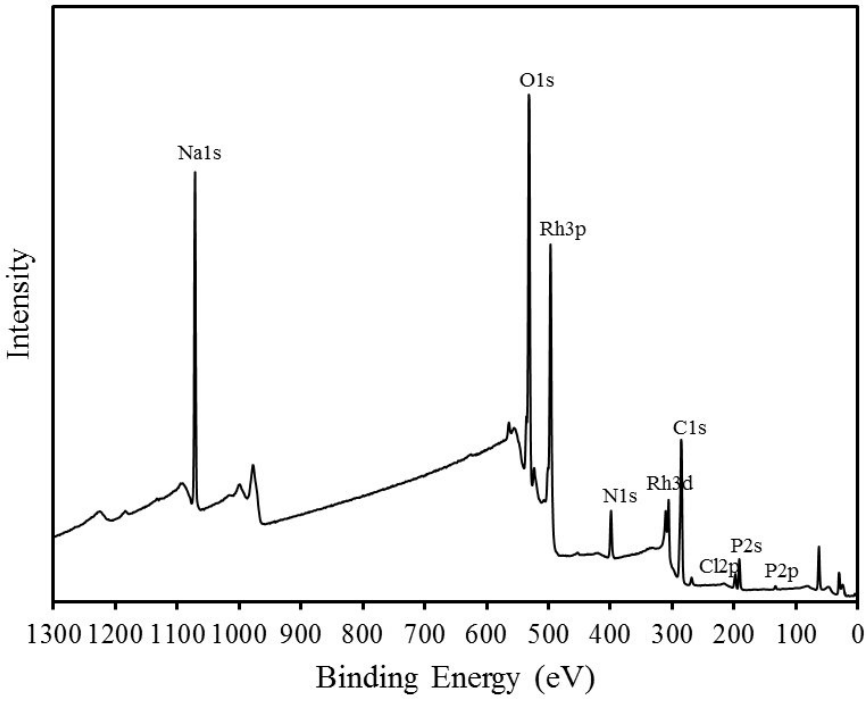


Figure S3. XPS survey scan of Rh/DNA nanowires formed by chemical reduction

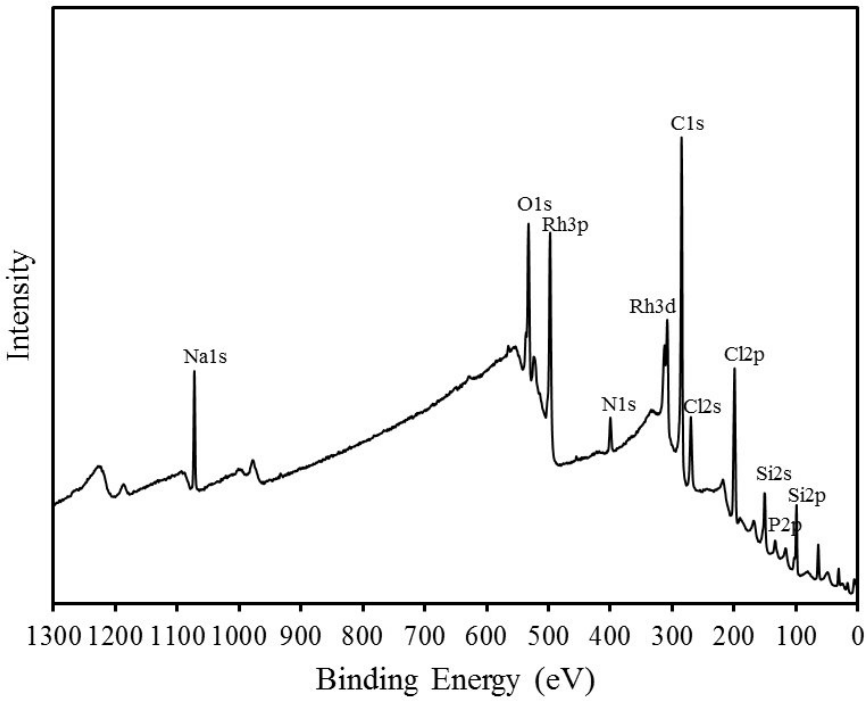


Figure S4. XPS survey scan of Rh/DNA nanowires formed by electrochemical reduction

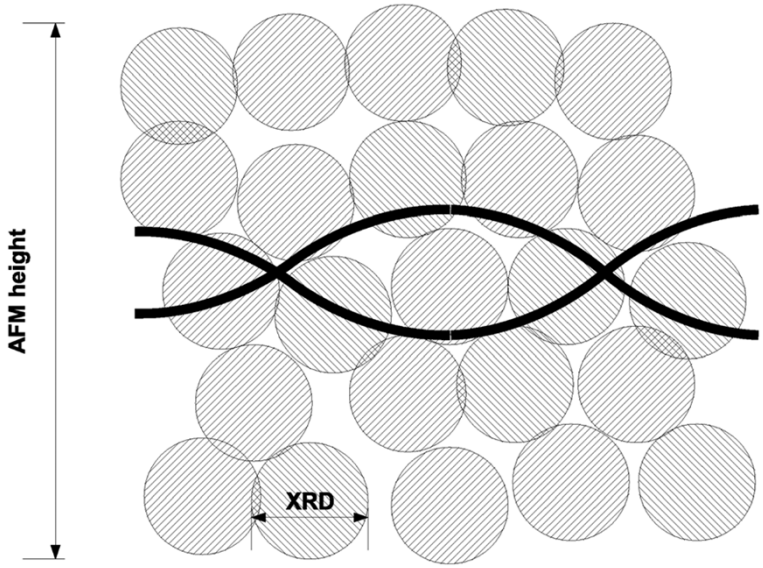


Figure S5. Schematic representation of the structure of the prepared DNA/Rh nanowires. The Rh crystallite size, indicated to be ~3 nm by powder XRD, is substantially smaller than the nanowire heights observed by AFM.

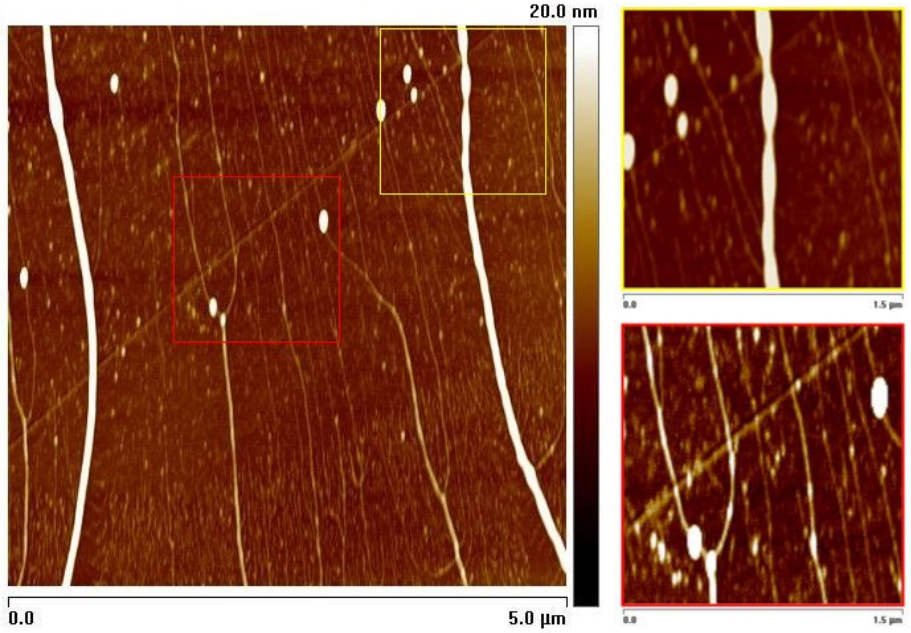
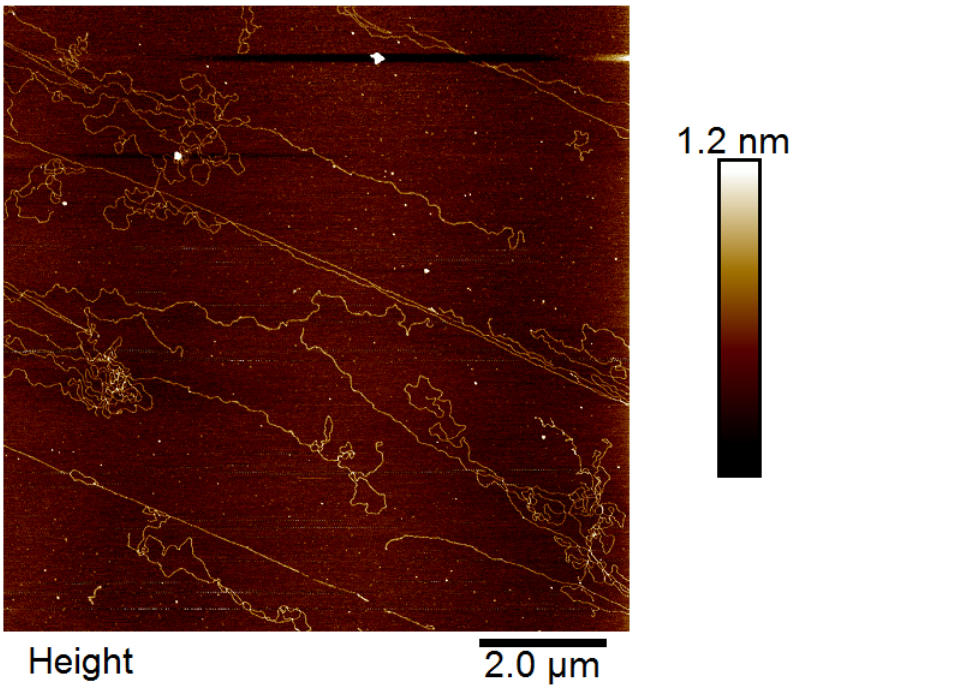


Figure S6. AFM height image for electrochemically-prepared Rh nanowires from Fig 5(b) and (right) expanded regions indicated by the yellow (top) and red (bottom) boxes highlighting "necking" and "particles-on-string" features

AFM analysis of λ-DNA



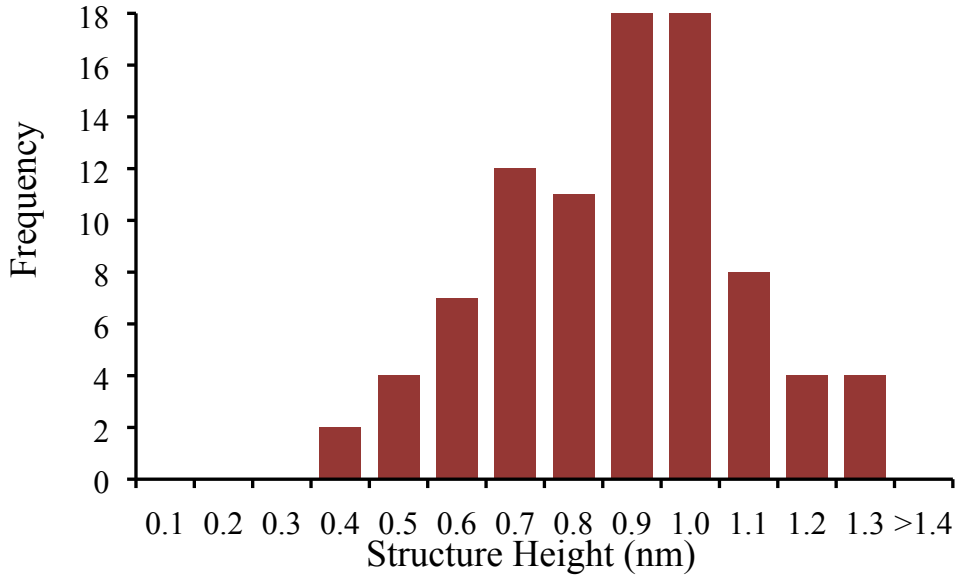


Figure S7. Tapping mode AFM of bare l-DNA deposited on mica and statistical analysis of the heights of the structures.

Scanned Conductance Microscopy (SCM) studies on DNA/Rh nanowires

Rh nanostructures prepared by either route were aligned *via* molecular combining upon Si/200nm SiO_2 substrates modified with a TMS monolayer. For the material synthesised by electrochemical reduction samples were prepared by transferring the reaction solution containing DNA/Rh "nanowires" from the Si working electrode to the TMS-modified Si wafer.

Figure S8 shows an AFM height image (Fig.S8(a)) of a DNA-templated Rh nanostructure *via* chemical reduction, indicating an average diameter of ~9nm, along with corresponding SCM phase images (Figure S8(b)-(e)), recorded at different applied bias potentials. Dark contrast can in seen in the phase images across the region of the nanowire, regardless of the bias value that is applied to the sample, indicating that they are electrically conductive.[4-6] This is further illustrated in Fig. S8(f), where the plot of the tangent of the nanowire phase shifts against the applied sample bias, show that the shifts are always negative and vary in magnitude as a function of the square of the applied bias (V^2). The observed negative phase shifts confirms that the structures display electrical conductivity, whilst the parabolic dependence of the magnitude of these shifts allows us to confirm that the phase shift do occur predominantly as a result of the capacitance effects of the probe-sample interactions, nor any alternative scenario such as the presence of static charges on the sample (where the phase shifts would be expected to show a linear dependence upon the applied bias).

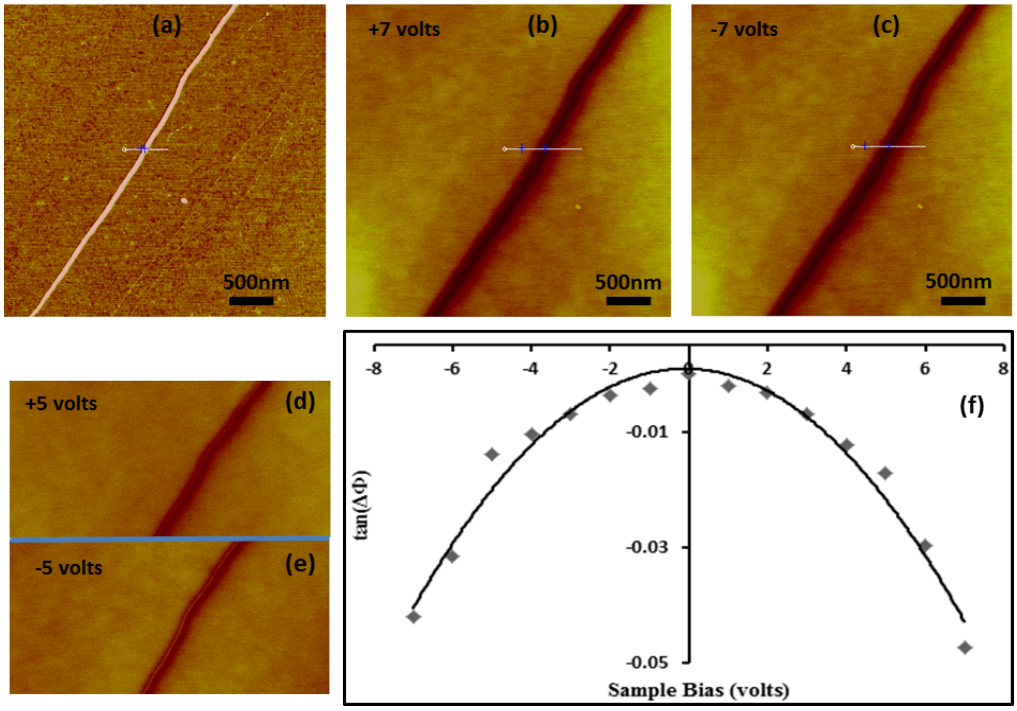


Figure S8. SCM studies carried out upon DNA/Rh_{Chem} nanowires (a) AFM height image, along with corresponding SCM phase images recorded at applied bias values of (b) +7volts, (c) -7volts, (d) +5 volts, (e) and -5 volts. (f) Plot of tangent of phase shifts vs. applied sample bias, illustrating the observed nanowire phase shifts demonstrate a parabolic dependence upon the applied bias value.

Figure S9a shows SCM data for the DNA/Rh_{Echem} nanostructures. The height image (Fig. S9a) reveals two main structures with diameters of 11 and 4.1 nm for nanowires denoted with yellow and green arrows, respectively. Bare DNA molecules (red arrow) can also be observed (heights <2 nm). The corresponding SCM phase images, collected during the second pass of the tip at a maintained tip-sample separation, with applied bias potentials of between +7 and -7 V, are shown in figure S9b and S9c, respectively. These images show negative phase shift associated only with the two larger structures. The negative phase shifts associated with these nanowires over the bias potentials range indicates that they are electrically conductive.[4-6] Furthermore, the tangent of the phase shift of nanowire (indicated with yellow arrow in height image) when plotted against the applied voltage (Fig. S9d) shows a parabolic curve, indicating that the tip-sample interactions are dominated by capacitance effects.

Figure S9: Height and EFM phase images of DNA/Rh_{Echem} nanowires immobilised upon Si/SiO_2 substrate. (a) Height image of the nanowires with different diameters (height scale is 10 nm). (b and c) The EFM phase images of the nanowires in (a) at sample biases of +7 and -7 Voltas, respectively, phase scale is 4°. (d) Plot of the tangent of the nanowire phase shift as a function of applied voltage.

Conducting AFM

Figure S10 shows an optical and AFM height images recorded at the periphery of the dense network deposit of Rh/DNA_{Chem} material on the substrate surface, and in which three separate DNA-templated Rh nanowires can be identified. The mean diameter of the main structures was found to be ~40 nm. This is notably larger than the typical size of these nanowires reported in the statistical analysis (Fig. 5, main paper). This suggests that the nanostructure seen here consists of DNA-templated Rh structure which have bundled together in a "rope-like" formation. Generally, it has been found difficult to image DNA-based structures of diameters smaller than this approximate size, in contact mode as in cAFM measurements. This is due to the high applied force of the AFM probe resulting in the probe having a tendency to readily displace smaller structures. Figure S10(c) shows the cAFM current map, acquired simultaneously to the height image, and in which a current signal can clearly be detected over regions correlating to points at which the AFM probe travels over the nanowires, again verifying the structures to electrically conducting.

Following acquisition of height/current data, an additional function of the cAFM mode was used to carry out i-V measurements in order to extract quantitative information regarding the nanowire's conductance. Here, the AFM probe was brought into contact at specific points along the length of the nanowire and i–V measurements recorded over the range of -5V to +5V. The nanowire resistance was subsequently estimated from the slope of the i–V curve around zero bias. It has previously been demonstrated that the information gathered in this manner can not only be used to determine the resistance per unit length of the nanowire, but also extract the contribution to the measured resistance from the probe–nanowire contact resistance.[7]

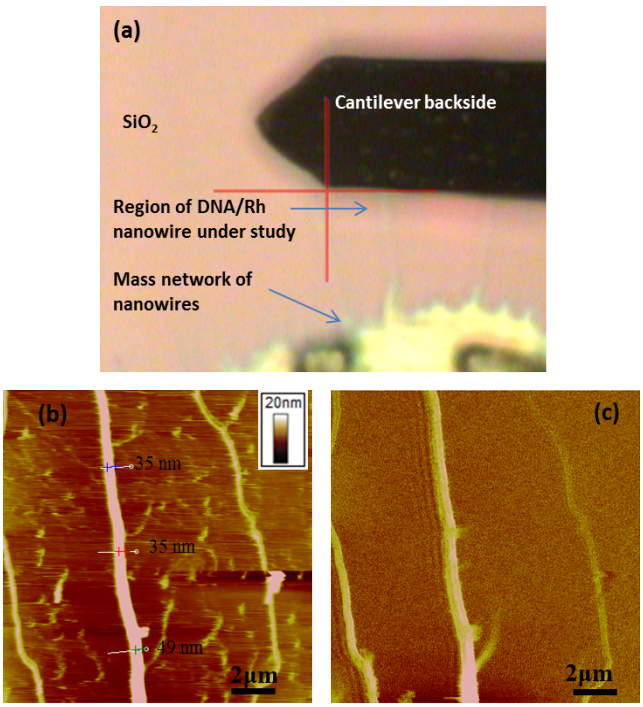


Figure S10. (a) Optical image illustrating key aspects of the experimental setup used here in order to carry out cAFM measurements upon the DNA-templated Rh nanowires. (b) Contact mode AFM height of a DNA-templated Rh nanostructure found at the periphery of the dense DNA/Rh material deposited upon the substrate support surface. (c) Corresponding cAFM

current image, recorded at 0.5V tip-sample bias and the data scale corresponds to a current of 100 nA, acquired simultaneously to the height image shown in (b).

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