Supporting Information:

High Electronic Conductance through Double Helix-DNA Molecules with Fullerene Anchoring Groups

Kathia L. Jiménez-Monroy\textsuperscript{1*}, Nicolas Renaud\textsuperscript{2*}, Jeroen Drijkoningen\textsuperscript{1,3}, David Cortens\textsuperscript{1}, Koen Schouteden\textsuperscript{4}, Christian van Haesendonck\textsuperscript{4}, Wanda J. Guedens\textsuperscript{1}, Jean V. Manca\textsuperscript{1,3}, Laurens D. A. Siebbeles\textsuperscript{2}, Ferdinand C. Grozema\textsuperscript{2} and Patrick H. Wagner\textsuperscript{1,5}

\textsuperscript{1}IMO-IMOMEC, Hasselt University, Campus Diepenbeek, Wetenschapspark 1, 3590 Diepenbeek, Belgium;

\textsuperscript{2}Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands; Hasselt University;

\textsuperscript{3}IMO & X-LaB, Agoralaan Building D, 3590, Diepenbeek, Belgium;

\textsuperscript{4}KU Leuven, Department of Physics and Astronomy, Solid-State Physics and Magnetism Section, Celestijnenlaan 200D, 3001 Leuven, Belgium;

\textsuperscript{5}KU Leuven, Department of Physics and Astronomy, Soft-Matter Physics and Biophysics Section, Celestijnenlaan 200D, 3001 Leuven, Belgium.

* Corresponding Authors Email: jimenezmonroy.kathia@gmail.com ; n.renaud@tudelft.nl
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1 Fulleren-DNA modification

The compounds, C60-CHCOOH (C61), N-Hydroxysuccinimide (NHS), and 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), were purchased from Sigma-Aldrich Co (ST. Louis, MO, USA). The DNA oligonucleotides (ssDNA) were purchased from Eurogentec (Liège, Science Park; Belgium). Our protocol is based on the work of Shin et al.1 to functionalise DNA-amine terminated strands with fullerenes. It is a two-step process, which consists of: i) DNA-fullerene modification, and ii) DNA-fullerene purification.

The single-stranded DNA oligonucleotides used for this experiment are:

- Forward (Fwd):

  5’-GGG GAC TCG CCA TTC ACC ATC CGC ACA GAA GTG ATG GGG GGC CCC GAG TCC CGC GGC GTC CTG CGC AAG ATG AGC GAC CTG CTG GAG CTG ATG GTG AAG CGC-3’-C₆H₁₃(CH₂OH)NH₂

- Backward (Bwd):

  5’-GCG CTT CAC CAT CAG CTC CAG CAG GTC GCT CAT CTT GCG CAG GAC GCC GCG GGA CTC GGG GCC CCC CAT CAC TTC TGT GCG GAT GGT GAA TGG CGA GTC CCC-3’-C₆H₁₃(CH₂OH)NH₂

First, the C60-CHCOOH (C61) was sonicated for 30 minutes in milliQ-water, and then centrifuged for 20 minutes at 4400 rpm. The well-dispersed supernatant solution (0.04 mg mL⁻¹) was sonicated for 30 minutes in the presence of EDC and NHS to form a labile intermediate. Then, the pH was raised to 7.2 and aminoalkyl-modified DNA oligonucleotides (Fwd and Bwd apart in separate tubes) in the presence of 0.15 M PBS were added to a final DNA concentration of 0.008 µg mL⁻¹. After performing the reaction at room temperature for 24 hours, the reaction mixture was centrifuged for 20 minutes at 5400 rpm to remove any type of aggregation.
2 DNA-fullerene purification
The supernatant fraction from the last centrifugation step was purified from the unreacted compounds, namely fullerenes, DNA and salts, using a dialysis method for 7 days at room temperature (molecular weight cut off (MWCO) = 12000-14000).

3 Characterisation

3.1 Ultraviolet-visible spectroscopy (UV-vis)
A NanoDrop 2000/ 2000c UV-vis spectrophotometer (Thermo Fisher Scientific Inc.) was employed to verify that no aggregation clusters (unreacted fullerenes) remain in the aqueous solution together with the functionalized DNA-fullerene (DNA-C61). Typically, for fullerene groups and derivatives\(^2\) that are suspended in aqueous solution, we expect a strong absorption peak between 215 - 257 nm, as it was observed at 220 nm in Figure S1a. One strong absorption peak appears with a broad shoulder around 260/280 nm, which is related to a neighboring covalently bound DNA. In the case of aggregated clusters, the signal at 220 nm would have been observed as a wide shoulder. Furthermore, the quantity and purity of the single strands of DNA-C61 (Fwd and Bwd) were determined using the absorption ratio \(\frac{A_{260 \text{ nm}}}{A_{280 \text{ nm}}}\). Figure S1b-c displays their spectra, from which we obtained the final amount of functionalized DNA-C61 in the solution. With this information, we were able to calculate the final reaction yield \(\left(\frac{ssDNA_{\text{DNA-C61}}}{ssDNA_{\text{C61}}} \times 100\% \approx 27\%\right)\).
**Figure S1** UV-vis spectra: (a) Measurement on DNA-C61 (at a range between 200 - 850 nm) shows a 220 nm peak corresponding to fullerene and a broad shoulder between 260 –280 nm is related to the DNA absorption (b-c) Analysis on ssDNA-C61 (Fwd and Bwd), where the 260/280 ratio gives information related to the final amount of functionalized DNA in the sample.

### 3.2 Fourier transformed- infrared spectroscopy (FT-IR)

We used a Bruker Tensor 27, Pike Miracle ATR cell (FT-IR) in order to confirm that an amide group was formed between the fullerene and the DNA (Figure S2). The spectra in Figure S2.a-b show several peaks due to a large number of aromatic bases (102 bp). In this figure, the transmission signal from the original non-modified strands (red line) is compared with C61 (black line) and the modified DNA-C61 strands (blue line). The main bands that are observed for “C61” correspond to the carboxylic group: C-OH and O=C-OH stretching at 3795.8 and 3325.1 cm\(^{-1}\) and O-H stretching at 2322.3, 2129.4 and 2013.6 cm\(^{-1}\)
from the strong hydrogen bond –COOH. The peak at 1612.5 cm\(^{-1}\) is attributed to the carboxylate anion stretch mode.

On the other hand, single stranded DNA presents several peaks related to the aromatic and phosphate groups in the sample. Both modified ssDNA-C61 moieties have bands at 3170.9 and 1713 cm\(^{-1}\) corresponding to an amide group. Also, a shift from the original C61 bands at 2322.3, 2129.4 and 2013.6 cm\(^{-1}\) was observed only in the case of modified DNA-strands: i) Fwd-C61 at 2368.5, 2191.1 and 2044.5 cm\(^{-1}\) and, ii) Bwd-C61 at 2175.7 and 1975.1 cm\(^{-1}\).

Figure S2| Transmittance vs. wave number FTIR spectra: (a) C61 (black), modified Fwd-C61 (blue) and non-modified Fwd single strand (red) are compared in the range between 4000-550 cm\(^{-1}\); (b) C61 (black), modified Bwd-C61 (blue) and non-modified Bwd single strand (red) are compared in the range between 4000-550 cm\(^{-1}\).
confirms the presence of the bands corresponding to a fullerene covalently attached to ssDNA (Fwd and Bwd) only for the modified samples of ssDNA-C61.

### 3.3 Hybridization and electrophoresis

After UV-vis and FT-IR confirmation of the DNA-fullerene modification, both DNA strands were allowed to hybridise in order to obtain only full-matched linear double-stranded DNA. The modified ssDNA strands were mixed in equimolar concentrations (buffer 0.1 M PBS), subsequently placed in a thermocycler and heated at 95°C for 2 minutes. Then, they were gradually cooled down to 25°C at a rate of 1.6°C min⁻¹. In order to verify the occurrence of only a single band of modified double-stranded DNA-C61, we loaded the samples to a 2% agarose gel (Figure S3) with a reference DNA ladder: GeneRuler 100 bp DNA ladder (Thermo Scientific Inc.). The Gelred (Biotium) dye was added to the gel to visualize the DNA and a constant voltage of 100 mV was applied to the gel for an hour (BIORAD Power Pac Basic Mini Sub Cell GT). From Figure S3, we confirmed that DNA-C61 displays one band per lane, at slightly higher molecular weight (MW) than the unmodified DNA (102 bp). It can be assumed that the small fullerene groups have an effect on the DNA migration and, as a consequence DNA-C61 appears at relatively higher MW. If not noted otherwise, these DNA-C61 samples (0.1 M PBS), were used for C-AFM and STM experiments.

![Gene Ruler 100 bp DNA ladder](image)

**Figure S3|Electrophoresis experiment in 2% agarose gel:** Left lane: GeneRuler 100 bp (Thermo Scientific). The unmodified DNA (red middle box) appears at a MW around 100 bp according to the Gene Ruler ladder (control).
Comparatively, DNA-C61 (red right box, experiment performed in double) has a slightly higher MW than unmodified DNA, as a result of the attached fullerenes.

3.4 Scanning probe microscopy
In order to obtain single molecules of DNA-C61, we diluted the original stock in milliQ-water, drop-casted it onto a flat gold surface and dried it under N₂ flow, yielding ~ 10 molecules per µm². The sample was left in a desiccator for 24 - 48 h before performing any type of measurement.

3.4.1 Atomic force microscopy (AFM)
We used a Bruker Multimode 8 AFM adapted inside a glovebox with a N₂ atmosphere and relative humidity less than 6%, with an internal Faraday cage compartment for the experiments with conductive-AFM (Figure S4-S6). For calibration, the first measurement was performed on a blank gold substrate, giving a steep Ohmic curve (Figure S4).

![Figure S4](image_url)

Figure S4| C-AFM on clean gold substrate, where a small gold area that is in contact with the AFM tip gives a contact-resistance value of 4.7 MΩ.

A control experiment was done using C61, solubilized in milliQ-water and deposited on gold. After 48 h in the desiccator, the sample was measured as shown in Figure S5, where consecutive series of bias
sweeps resulted in a non-linear $I(V)$ curve, with an average voltage gap of about 1.5 eV between -2 to +2 V, as seen in Figure S5f. Furthermore, Figure S5b illustrates the area where the AFM tip was located during the time of the measurement, seen as a hole on the original cluster. At the end of the measurement, we assume that some C61 molecules might have attached to the AFM tip, resulting in a lower resolution of the image compared to Figure S5a.

**Figure S5** C61 deposited on gold. (a-d) Contact-AFM height image of 0.4 x 0.4 μm$^2$ size with corresponding line profiles, before (left) and after (right) the C-AFM experiment. (e-f) The left set of C-AFM curves started with fluctuations between -3 to +4 V bias voltages and reached a final reproducible non-linear curve between ± 2 V.
Then, C-AFM measurements performed on DNA-fullerene molecules are displayed in Figure S6.a-c, where all curves belong to different positions on one molecule. Further C-AFM experiments were performed on additional DNA-C61 molecules (a total of 22 single molecules) at different starting positions, thereby confirming the high conductance trend in 19 out of 22 (86%) experiments. Conductance along the DNA molecule seems to be influenced by the DNA sequence\(^4\) (see Figure S7 and Table S1), especially for the T10 position. At this position, we assume that the AFM tip is in contact with four base pairs, in this case three A/T pairs, which results in a lower conductance compared to the previous position T9 (two A/T pairs). This lower conductance could be related to an intermediate tunnelling-hopping regime described earlier in literature, depending on the base pair sequence\(^3,4\).
**Figure S6| C-AFM (a- c)** Top-middle-bottom direction: All thirty IV curves corresponding to the AFM tip positions of DNA-C61 deposited on a gold substrate. Note the slope change when the AFM tip is moved from the middle position of DNA-C61 (T1) towards the fullerene end of the molecule (T30).

**Figure S7| DNA sequence vs AFM tip position.** Example of the DNA sequence where the AFM tip injected charges at positions T1, T9 and T10 (within the same molecule). A clear decrease of conductance is observed particularly for T10 during the measurement.

**Table S1| Conductance (dI/dV) values.** For each measured I-V curve (T1-T30), the conductance was calculated, as shown below. Here, D is the distance between the tip and the fullerene end.
Finally, we tested the effect of removing all salts from the DNA-fullerene structure by means of a gel extraction kit (Agarose Gel DNA extraction kit, Roche Diagnostics) and final dilution in milliQ-water. The results are displayed in Figure S8 and Figure S9, where the molecule dimensions have changed to height and length values of ~ 5.4 nm and ~ 31 nm respectively, as well as the conductance values (Table S2), which in this case are about 10-100 times lower compared to the standard DNA-C61 molecules (Table S1). This could be attributed to disturbances in π-π stacking and change of distances between base pairs, where no salt is involved in stabilising the structure in an inert environment.

Figure S8| Contact-AFM image of 0.3 x 0.3 µm² size. (a) Height image of a desalted DNA-fullerene molecule deposited on top of gold and (b) Line profile of the molecule, from where the height and length was measured to be of 5.4 nm and 31.7 nm respectively.
Figure S9 | C-AFM. (a-b) Desalted DNA-C61 deposited on a gold substrate. Here, higher voltage ranges (± 2 V) were applied to the desalted DNA-C61 molecules. Nevertheless, the measurement shows 20 times lower currents than the standard DNA-C61 molecules as shown e.g. in Figure S5.
**Table S2| Conductance (dI/dV) values for desalted DNA-C61.** For every measured I-V curve (T21-T30 and final position on gold), the conductance was calculated, as shown below.

|     | D (nm) | dI/dV (S) |
|-----|--------|-----------|
| T21 | 6.475  | 7.48E-15  |
| T22 | 5.825  | 1.09E-14  |
| T23 | 5.175  | 1.91E-13  |
| T24 | 4.525  | 1.52E-12  |
| T25 | 3.875  | 1.90E-11  |
| T26 | 3.225  | 1.58E-10  |
| T27 | 2.575  | 9.27E-10  |
| T28 | 1.925  | 3.64E-09  |
| T29 | 1.275  | 8.88E-09  |
| T30 | 0.625  | 1.33E-08  |
| Au  | -0.025 | 1.29E-08  |

An important feature in this experiment is the strong coupling between C61 and the gold surface, which forms the electrode. After DNA functionalization, charge injection from the last base pair connected to C61 appears to be at an energy close to the Fermi energy of the electrode. This effect was observed despite the absence of salts in the DNA structure and was confirmed in theoretical calculations discussed, here in section 5.

### 3.4.2 Scanning tunnelling microscopy (STM)

The STM experiments (Omicron NanoTechnology) were performed under ultrahigh vacuum (base pressure below 5 x 10^{-11} hPa) and at room temperature. For these measurements we used Au (111) substrates prepared at KU Leuven and tips of Pt-Ir (10% Ir). Figure S10 illustrates that when DNA-C61 molecules are deposited on the gold substrate, they aggregate at the big step edges of gold. It appears that DNA-C61 do not present a stable mechanical contact with the surface. As a consequence, Figure S10b shows noise in the scan lines, related to the displacement of the DNA-C61 molecules. Therefore, DNA do no present a coherent\(^5\) nor a transverse\(^6\) tunnelling behaviour and the molecules were only displaced along the surface by means of the Pt-Ir tip.
Figure S10|Scanning tunnelling microscopy. Before annealing: DNA-C61 molecules appear to aggregate, observed at (a) Z-height scale: 38 nm and (b) Z-height scale: 50 nm, where the molecules seem to move along with the Pt-Ir tip.

In order to increase the image resolution and the interaction between C61 and the gold surface\(^7\), it was necessary to anneal the samples (internal heater was brought to 350°C) and then decrease the setup measuring temperature to 78 K. Unfortunately, this annealing induced DNA damage as shown in Figure S11. Here, a clean gold substrate can be seen in the background pattern and small spherical structures (C61) are surrounded by burned organic material (DNA).

Figure S11|Scanning tunnelling microscopy. After annealing, Z-height scale is 0.5 nm for both (a) and (b). After annealing, we observed burned or decomposed organic material (yellow arrow) surrounding the C61 molecules (blue circles) on top of a very clean gold surface (red arrow), seen in the characteristic herringbone ridge pattern of (111) oriented gold surfaces.
4 Theoretical model of incoherent transport (multistep charge hopping)

4.1 Model without direct injection

We present here the details of the kinetic model used to simulate our experimental results. The main assumption is that charge transport occurs via a sequence of incoherent hopping steps between neighboring sites. The one-dimensional kinetic hopping model represented in Figure S12 was employed to describe this mechanism. In this figure tip/surface represent the electron reservoirs in the tip and surface respectively. The different sites between the tip and the surface represent the base pairs along the DNA structure. Due to the possible delocalization of the electronic wave function, these sites can correspond to several base pairs. We assume that all these sites are identical.

![Model](image.png)

Figure S12| Model. Representation of the kinetic model used to simulate the transport of charge along the DNA structure.

As mentioned in the main text, the injection rates from and to the DNA were calculated using the theory of electron-transfer electrochemistry. The injection and extraction rates between the tip and the first site of the DNA are given by:

\[
 k_{\text{tip}}(V) = c_{\text{tip}} \int_{-\infty}^{\infty} dx \, \exp \left[ - \left( \frac{\lambda + \delta + \alpha_{\text{tip}} eV}{k_B T} \right) \left( \frac{k_B T}{4 \lambda} \right) \right] (1 + e^x)^{-1}
\]  

(Equation S1)
\[ k_{\text{tip}}^\leftarrow (V) = c_{\text{tip}} \int_{-\infty}^{\infty} dx \ exp \left[ - \left( x - \frac{\lambda - \delta - a_{\text{tip}} eV}{k_B T} \right)^2 \left( \frac{k_B T}{4 \lambda} \right) \right] \left( 1 + e^x \right)^{-1} \quad (\text{Equation S2}) \]

Similarly the injection and extraction rate between the last site of the DNA and the surface are given by:

\[ k_{\text{surf}}^\leftarrow (V) = c_{\text{tip}} \int_{-\infty}^{\infty} dx \ exp \left[ - \left( x - \frac{\lambda + \delta - a_{\text{surf}} eV}{k_B T} \right)^2 \left( \frac{k_B T}{4 \lambda} \right) \right] \left( 1 + e^x \right)^{-1} \quad (\text{Equation S3}) \]

\[ k_{\text{surf}}^\rightarrow (V) = c_{\text{tip}} \int_{-\infty}^{\infty} dx \ exp \left[ - \left( x - \frac{\lambda - \delta + a_{\text{surf}} eV}{k_B T} \right)^2 \left( \frac{k_B T}{4 \lambda} \right) \right] \left( 1 + e^x \right)^{-1} \quad (\text{Equation S4}) \]

As mentioned in the main text, the forward and backward rates are given by:

\[ k_f = k_0 e^{-\frac{a_{\text{mol}} eV}{3(N-1)k_B T}} \quad \text{and} \quad k_b = k_0 e^{\frac{a_{\text{mol}} eV}{3(N-1)k_B T}} \quad (\text{Equation S5}) \]

The kinetic model is then given by the system of linear equations:

\[ \dot{P}_1 = -(k_{\text{tip}}^\leftarrow + k_f)P_1 + k_b P_2 + k_{\text{tip}}^\rightarrow P_{\text{contact}} \quad (\text{Equation S6}) \]

\[ \dot{P}_n = -(k_b + k_f)P_n + k_b P_{n-1} + k_f P_{n+1} \]

\[ \dot{P}_N = -(k_{\text{surf}}^\leftarrow + k_f)P_N + k_f P_{N-1} + k_{\text{surf}}^\rightarrow P_{\text{contact}} \]

where \( P_i \) represent the population of the \( i \)-th site, and \( P_{\text{contact}} \) represent the population of the tip and the surface. To solve this system we use the steady state limit where all the derivative are set to 0: \( \dot{P}_i = 0 \).

This system of equation can be written conveniently in matrix form:

\[ M \times P = b \quad (\text{Equation S7}) \]

with:
\[ M = \begin{pmatrix}
-(k_{\text{tip}} + k_f) & k_b & 0 & \cdots & k_{\text{tip}} \\
k_f & -(k_b + k_f) & k_b & \cdots & 0 \\
\vdots & \vdots & \ddots & \cdots & \vdots \\
0 & \cdots & k_f & -(k_{\text{surf}} + k_f) & k_{\text{surf}} \\
1 & \cdots & 1 & 1 & 1
\end{pmatrix} \]

The last line of this equation comes from the normalization condition \( P_1 + P_2 + \cdots + P_N + P_{\text{contact}} = 1 \). This equation is then solved numerically by computing \( P = b \setminus M \). This solution provides the values of the population of the different states in the steady state limit. The intensity of the current flowing through the DNA is then calculated by:

\[ I_{\text{tip}}(V) = -e \left( k_{\text{tip}} P_{\text{contact}} - k_{\text{tip}} P_1 \right) \quad \text{(Equation S9)} \]

\[ I_{\text{surf}}(V) = -e \left( k_{\text{surf}} P_N - k_{\text{surf}} P_{\text{contact}} \right) \]

These two currents are identical in the steady state limit. The software used to compute the current is available from the authors on request. This model was used to reproduce the experimental \( I(V) \) curves as represented in Figure 5a of the main text.

### 4.2 Model with direct injection

A direct injection from each base pair to the surface was then introduced in the model described above to evaluate to possibility of direct charge transfer between the DNA to the surface. This model is similar to the one described by Equations S8 with additional terms in the matrix \( M \):

\[ M = \begin{pmatrix}
-(k_{\text{tip}} + k_f) & k_b & 0 & \cdots & k_{\text{tip}} \\
k_f & -(k_b + k_f + k_1^-) & k_b & \cdots & 0 \\
\vdots & \vdots & \ddots & \cdots & \vdots \\
0 & \cdots & k_f & -(k_{\text{surf}} + k_f) & k_{\text{surf}} \\
1 & \cdots & 1 & 1 & 1
\end{pmatrix} \quad \text{(Equation S10)} \]
As seen in this equation each site now interacts with the surface via the terms: $k_{i}^{\text{inout}}$. This injection and extraction rates between the base pair and the surface were calculated as the ones given in Equation S1-S4:

$$k_{i}^{\text{in}}(V) = c_{\text{direct}} \int_{-\infty}^{\infty} dx \, \exp \left[ - \left( x - \frac{\lambda + \delta - E_i}{k_b T} \right)^2 \left( \frac{k_b T}{4 \lambda} \right) \right] \left( 1 + e^x \right)^{-1}$$  \hspace{1cm} (Equation S11)

$$k_{i}^{\text{out}}(V) = c_{\text{direct}} \int_{-\infty}^{\infty} dx \, \exp \left[ - \left( x - \frac{\lambda - \delta + E_i}{k_b T} \right)^2 \left( \frac{k_b T}{4 \lambda} \right) \right] \left( 1 + e^x \right)^{-1}$$  \hspace{1cm} (Equation S12)

where $E_i$ is the on site energy of the i-th base pair that takes into account the voltage drop between the two electrodes. As an illustration we show on Figure S13 typical $I(V)$ curves obtained with this model for $c_{\text{direct}} = 10^{10} \text{ s}^{-1}$. As can be seen in this figure the calculated $I(V)$ curves present pronounced non-linearity that are not observed experimentally.

Additionally, this direct injection rates leads to a distance dependence of the conductance that is weaker than the one observed experimentally. This is clearly observed in Figure S14, which strongly suggests that such direct injection plays a minor role in the charge transfer along our DNA molecules.
Figure S13 | Direct injection. I(V) curves obtained in presence of direct injection between the base pair and the surface.

Figure S14 | Direct injection. Distance dependence of the conductance. The open black dots represent our experimental results and the blue line our theoretical results without direct injection. The purple line shows the conductance when the direct injection rate is taken into account.

5 Theoretical model of coherent transport (tunnelling charge transport)

Since the substrate is metallic, charge transport can in principle occur vertically through the molecule without involving the propagation of charges along the entire DNA sequence. To assess the importance of this mechanism we have calculated the intensity of the tunneling current obtained in the junctions shown in Figure 3. In these junctions the AFM tip and gold surface are modeled by clusters containing 126 and 230 gold atoms respectively. To limit the calculation time, a short sequence of DNA containing only 3 base pairs was placed within the junction. This molecule was positioned 0.3 nm away from the surface. A
similar distance separates the molecule from the model AFM tip. The tunneling current was computed in the Landauer formalism:\(^9\):

\[
I(V) = \frac{2e}{\hbar} \int_{-\infty}^{\infty} dE \ T(E) \left[ f\left(E - \frac{eV}{2}\right) - f\left(E + \frac{eV}{2}\right) \right]
\]

where \(T(E)\) is the transmission coefficient through the junction and \(f\) the Fermi function\(^{10}\). The electronic structure of the junction was calculated using the extended-Hückel theory\(^{11}\). The transmission coefficients were calculated using the Green function approach\(^{12}\):

\[
T(E) = Tr \left[ \Gamma_L G^a(E) \Gamma_R G^r(E) \right]
\]

where \(\Gamma_{L/R}\) represent the coupling between the molecule and the left/right electrode and \(G^{a/r}(E)\) are the advanced/retarded Green functions of the junction. We have first applied this method to an isolated fullerene as represented in Figure S15. As seen on this figure the \(I(V)\) curve obtained with our simulations (Figure S15c) closely resemble the experimental curve shown in Figure S5f. These results validate our theoretical approach. The electronic coupling between the HOMO of the fullerene and the electronic states was extracted from our calculations. As seen in Figure S15d, the fullerene is strongly coupled to the surface with electronic coupling ranging between 10-100 meV at a distance of 3.4 Å.
**Figure S15** Coherent transport through a model fullerene junction. **a)** Representation of the junction and HOMO of the sequence. **b)** Transmission coefficient of the junction. **c)** Tunneling current intensity obtained for the junction (plane line) and with a shift of -1 eV of the Fermi energy (dashed line). **d)** Electronic coupling between the HOMO of the molecule and the electronic states of the tip and of the surface.

Then, we have computed the tunneling current intensity obtained for different model DNA sequence containing 3 base pairs. Two extreme cases, namely CGC and TAT were considered. The results of these calculations are shown in Figure S16 and Figure S17. The I(V) curves reported in these figures shows a large voltage gap. The extension of this gap depends on the exact level alignment between the Fermi energy of the electrode and the orbitals of the molecule. However, even if the Fermi energy is brought close to the HOMO energy of the DNA sequence, the gap exceeds 2 eV. This is due to the fact that the HOMO of the sequence is localized on the p-orbitals of the base pairs (Figure S16a and Figure S17a). This localization leads to very weak coupling between the HOMO of the sequence and the electronic states of the electrodes (Figure S16d and S17d). The conducting channels creating the pronounced resonance of the transmission coefficient and therefore supporting the tunneling current are mainly composed of $\sigma$ orbitals of the base pairs coupled to orbitals from the backbone and are therefore deeply buried below the HOMO of the sequence.
**Figure S16** Coherent transport through a model GCG DNA sequence. a) Representation of the junction and HOMO of the sequence. b) Transmission coefficient of the junction. c) Tunneling current intensity obtained for the junction (plane line) and with a shift of -1 eV of the Fermi energy (dashed line). d) Electronic coupling between the HOMO of the molecule and the electronic states of the tip and of the surface.

**Figure S17** Coherent transport through a model ATA DNA sequence. a) Representation of the junction and HOMO of the sequence. b) Transmission coefficient of the junction. c) Tunneling current intensity obtained for the junction (plane line) and with a shift of -1 eV of the Fermi energy (dashed line). d) Electronic coupling between the HOMO of the molecule and the electronic states of the tip and of the surface.


6 Charge Transfer Mechanism

The Landau-Zener theory states that the probability for electron transfer between an initial and final state is given by:

\[ P_{I \rightarrow F} = 1 - \exp (-\gamma_{ZL}) \]

If both the initial and final states are delocalized over \( N \) identical states, with the Landau-Zener parameter given by:

\[ \gamma_{ZL} = \frac{1}{N^{3/2}} \frac{\pi^{3/2} V_{FI}^2}{\hbar \omega \sqrt{\lambda_{FI} k_B T}} \]

where \( V_{FI} \) is the electronic coupling between the individual states, \( \lambda_{FI} \) the reorganization energy of the reaction and \( \omega \) the average phonon frequency that triggers the electron transfer. The determination of the Landau-Zener parameter gives an indication about the nature of the charge transfer mechanism. If \( \gamma_{ZL} < 1 \) we have a non-adiabatic transfer whereas \( \gamma_{ZL} > 1 \) indicates an adiabatic transfer. In the case of DNA several studies have shown that \( V_{FI} \approx 50 \) meV and that \( \lambda_{FI} \approx 0.5 - 1.0 \) eV. Considering an average phonon frequency of 1 ps\(^{-1}\) and keeping the value \( N = 4 \) leads to \( \gamma_{ZL} \approx 2.6 - 3.7 \). The charge transfer is therefore likely to be non-adiabatic. In that case the charge transfer rate is largely coupling independent and is given by:

\[ k = \frac{\omega}{2\pi} \exp \left(-\frac{\Delta G}{k_B T}\right) \]

with

\[ \Delta G = \frac{(\Delta G_0 + \frac{\lambda_{FI}}{N})^2}{4 \lambda_{FI} / N} - \frac{|V_{FI}|}{N} \]

where \( \Delta G_0 \) the free energy gap of the reaction. In the limit of \( \Delta G_0 = 0 \), which corresponds to identical sites, these expression lead to value of \( k \) ranging between \( 2.0 \times 10^{10} \) s\(^{-1}\) and \( 8.0 \times 10^{10} \) s\(^{-1}\). For comparison our fit of the charge transfer lead to a value of the unbiased charge transfer rate of \( k = 2.3 \times 10^{11} \) s\(^{-1}\). This is not
so far off the predicted values obtain from the non-adiabatic expression of the charge transfer rate. Note that an increase of the charge transfer integral to $V_{FL} \approx 50$ meV leads with $\lambda_{FL} = 0.5$ to $k = 2.0 \times 10^{11}$ s$^{-1}$. Similarly keeping $V_{FL} \approx 50$ meV but decreasing the reorganization energy to $\lambda_{FL} = 0.25$ leads to similar values of the charge transfer rate.

In the case of the injection from the tip to the DNA molecule we however have $V_{FL} \approx 1$ meV and $\lambda_{FL} \approx 85$ meV. The first value comes from the calculations shown in Fig. S16 - S17 and the latter from the fit of the experimental results (Table 1). Note that these values already account for the delocalization of the charge. In this case we have $\gamma_{ZL} < 1$ and the transfer is therefore non-adiabatic. The charge transfer rate is then given by:

$$k = \frac{\pi}{\lambda_{FL} k_B T} \frac{V_{FL}^2}{\hbar} \exp \left( - \frac{\Delta G}{k_B T} \right)$$

with

$$\Delta G = \frac{(\Delta G_0 + \lambda_{FL})^2}{4\lambda_{FL}}$$

Using the values reported in Table 1 and here this leads to a charge transfer rate of $k \sim 10.0 \times 10^9$ s$^{-1}$ only one order of magnitude lower than the value of $c_{tip}$ and $c_{surf}$ that are both equal to $10 \times 10^{10}$ s$^{-1}$. However an increase of the coupling parameter to just 3 meV leads to a value of $k \sim 7.0 \times 10^{10}$ s$^{-1}$.

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