Supporting information for: Boosting DNA Recognition Sensitivity of Graphene Nanogaps through Nitrogen Edge Functionalization

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Geometrical distances

Table S1 shows the distances d_1 (d_2), described in Figure 1 of the main manuscript. There are two types of nucleobases considering the number of rings in each molecule. Nucleobases A and G (type I) have two rings, and C and T (type II) have just one. The distances d_1 and d_2 follow these two groups after geometry relaxation. For both devices, H and N edge passivation, the nuclobase of type I shows smaller distance compared with type II. The G(T) nucleobases are larger(smaller), and this fact is also reflected on the distance for both devices.

Table S1: Nucleobase distances in units of Å relative to the left (d_1) and right(d_2) edges of the X-terminated graphene sheet (X={H,N}) as defined in Figure 1 of the main manuscript.

Nucleobase	Hydrogen edge		Nitrogen edge	
	d_1	d_2	d_1	d_2
A	2.104	2.624	1.977	2.492
C	2.170	3.099	2.004	2.952
G	1.857	2.661	1.741	2.363
T	2.217	3.264	2.126	2.982

Sensitivity comparison

Table S2: Zero-bias conductance in units of the quantum conductance, G_0 =$2e^2/h$, for different nucleobases placed in a graphene nanogap with edges terminated either by H (left column) or N atoms (right column).

Nucleobase	Conductance (G_0)	
	H	**N**
G	8.88×10^{-10}	3.24×10^{-5}
A	1.09×10^{-10}	6.05×10^{-6}
C	3.24×10^{-11}	1.36×10^{-7}
T	2.35×10^{-13}	6.51×10^{-8}

Table S2 shows the zero bias conductance for H and N edge functionalization. We note a conductance boosting of four(five) orders of magnitude for A and C (G and T).

In figure S1 we present the sensitivity of each base for different energies. In the main manuscript (Figure 5f) the sensitivity is presented only for $E = E_F$. The results presented in Figure S1 shows the sensitivities for different gate voltages applied. We used the nucleobase T as a reference because it exhibits the smallest transmission. The selected voltages correspond to the transmission resonances for each nucleobase, and it is possible to distinguish each nucleobase.

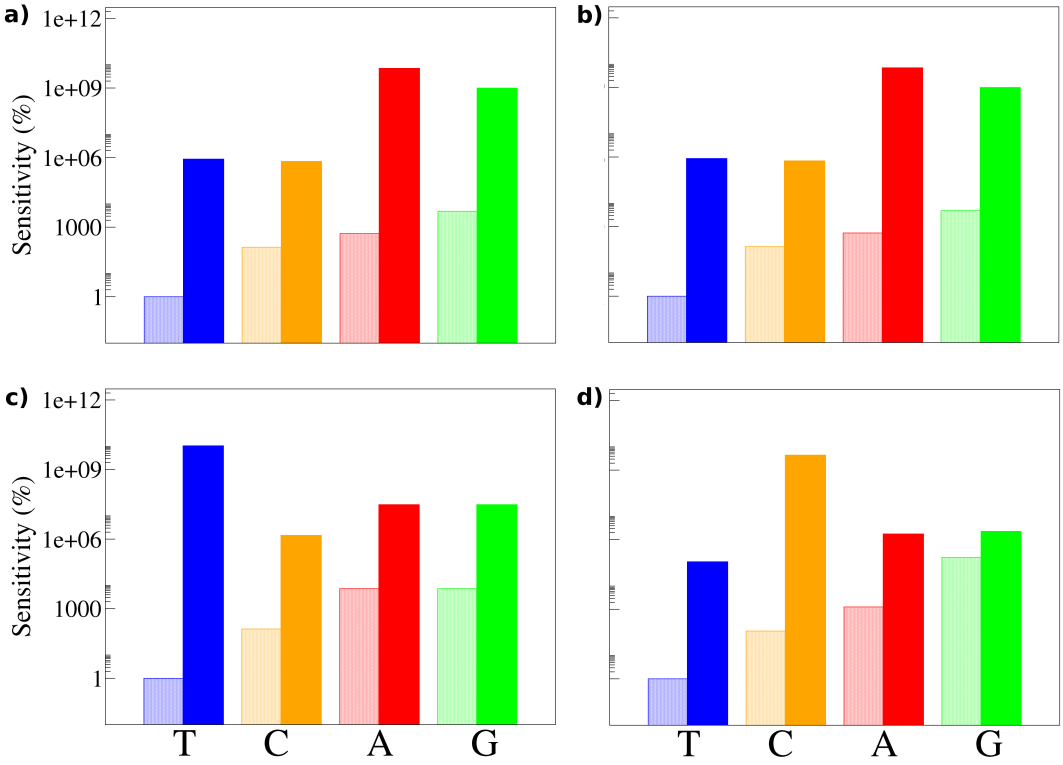

Figure S1: Sensitivity for A, C, G and T considering two devices and the smallest conductance as reference (i.e., nucleobase T at H-functionalized edge). The faint color bars correspond to H-functionalized edges while the full color bars represent data from N-functionalized edges. We examined four gate voltages corresponding to the transmission peaks of each nucleobase at N-funcionalized edge device: a) $V_g = 0.05$ V; b) $V_g = 0.07$ V; c) $V_g = 0.16$ V and d) $V_g = 0.42$ V.

We have also calculated the $I - V$ characteristics for the different nucleobases using a Buttiker-Landauer approach where the current

$$I(V) = \frac{2e}{h} \int T(E) \left(f_L(E) - f_R(E) \right) dE \ , \tag{1}$$

and $f_{L/R} = \frac{1}{1+e^{(E-\mu_0 \mp V/2)/k_B T}}$ is the Fermi-Dirac distribution function for left/right electrodes with chemical potential $\mu_0 \pm V/2$. The result is shown in Figure S2.

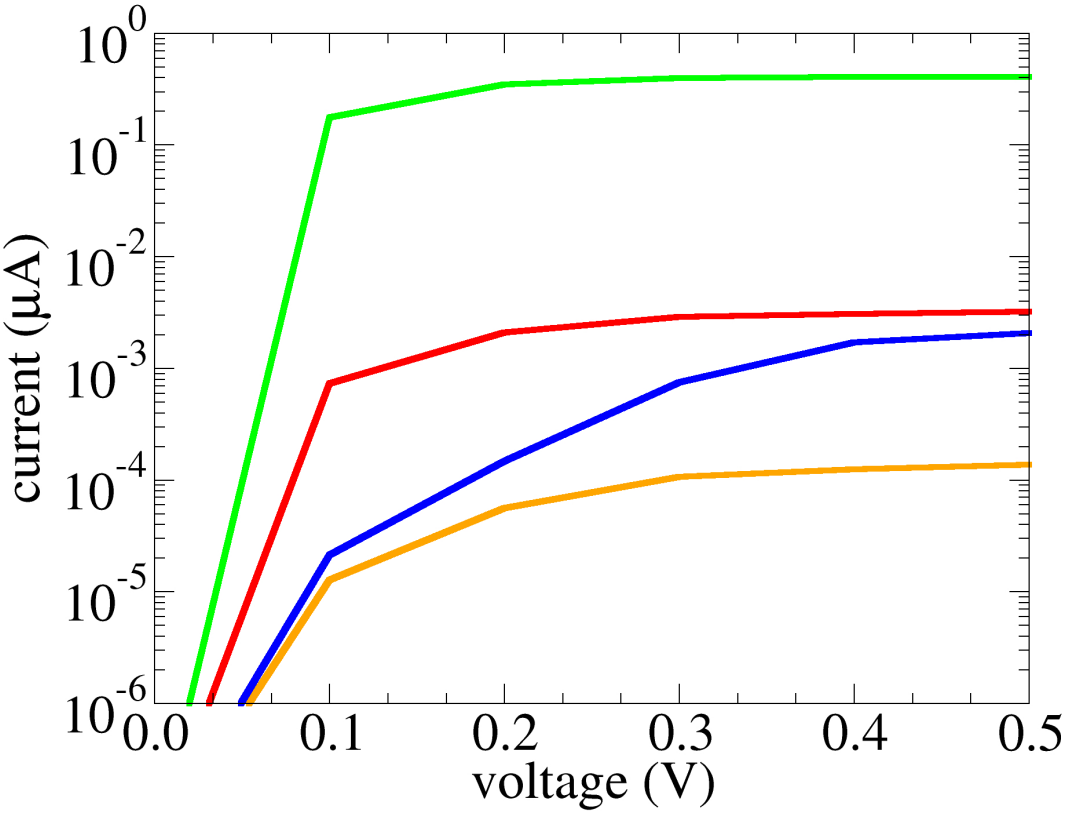

Figure S2: Current-voltage characteristics for the different nucleobases inside the N-terminated nanogap.

Figure S2 shows (I-V) curve for small applied bias. We note for ($V < 0.1$ V), that C and G are distinguishable and C and T are very similar. However, for ($V > 0.1$ V) each nucleobase has a distinct signature, leading them to become distinguishable.

Nucleobase rotation

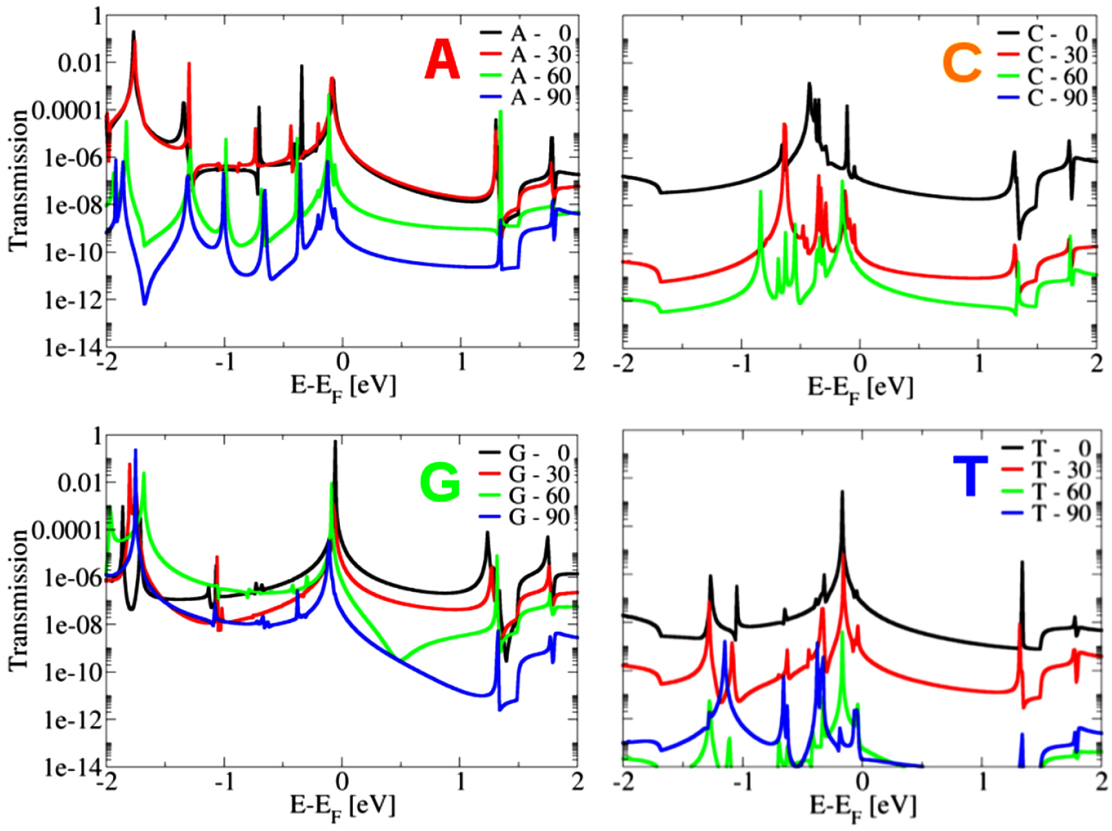

Figure S3: Transmission as a function of energy for different nucleobases and different rotation angles as defined in Figure 1 of the main manuscript. The lowest energy configuration corresponds to 0^o. Due to time reversal symmetry and mirror symmetry between left and right electrodes, only one quadrant is required. For cytosine at 90^o, the transmission is significantly smaller, and is thus, not shown

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In figure S3 we present the transmission for each nucleobase at the equilibrium height($z = 0$ Å) for different rotation angles with respect to the axis perpendicular to the graphene plane. Due to time reversal symmetry and mirror symmetry between left and right electrodes, only one quadrant is required. As a general trend, rotating the structure away from the lowest energy configuration the conductance is significantly reduced the conductance.