PAPER

Supplementary information for "Peptide bonds detection via graphene nanogaps: a proof of principles study"

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S1 ZGNR transport in water environment

We have calculated the transport properties of the nanostructures here considered taking into account the possible influence of water molecules. First we have considered the case of the ZGNR with a close layer of water molecules. This configuration has been fully relaxed with the Quantum Espresso package (the force and energy threshold smaller than the ones specified in the Theoretical methods section of the main text in order to get the ground state configuration that, in principles, should be the ones with water molecules better adapted close to the GNR. In Fig. S1(a) we report the transmission function in the relevant energy range of the hydrated ZGNR as compared to the dry one: the two curves are practically indistiguishable. As a second issue, we have optimized the configuration of one single water molecule in the middle of the nano-gap. we have found that in the ground state configuration, where also the current signal is maximum, the water molecule is just above the ZGNR plane. The transmission function and the current measured in this case have been compared to the one of the global minimum of the PB current signal measured for a Gly homo-peptide, as reported in Fig. S1(b). We see that the signal measured in this case is well below the minimum transmission function obtained with the Gly side chain in the nano-gap. The measured current value is $I_{\rm SC} \approx 0.15 \, nA$ that is about one order of magnitude lower that the maximum signal measured in the Gly homo-peptide and well below the absolute minimum signal with the side chain in the gap $I_{\rm SC} \approx 0.4 \, nA$

S2 Projected density of states of Gly-Gly PBs

In order to evidence in more detail the role of the PB atoms and orbitals, we have analyzed the orbital PDOS of the PB atoms for the $(NH)_i$ and the $(CO)_i$ configurations corresponding to the four current peaks of Fig. 2. The main findings are reported in Fig.??. In all the configurations, we see that the leading role is played by the p_z orbitals of N and C and, at a lesser extent and different way for $(NH)_i$ and $(CO)_i$, by the O_{p_z} and O_{p_x} orbitals. For the $(NH)_i$ cases, we see that that all the PDOS of the p_z orbitals involved in the PB resonant double bond rise approximately at 0.2 eV, where the transmission coefficient starts to increase too. However some differences between the two PBs can be noted: while the p_{z} density rises above the Fermi energy $(E_{\rm F} = 0 \, eV)$ for all the atoms involved in the PB in the $(NH)_1$ case, in the $(NH)_2$ case we see a major role of N_{p_z} above the Fermi energy and a larger PDOS of C_{p_z} and O_{p_z} below the Fermi energy. This means that conduction (related to the density above $E_{\rm F}$) may concentrate differently in the double bond depending on the fluctuations of the atomistic configurations. Concerning $(OH)_i$ we observe that the empty states above $E_{\rm F}$ have a predominance of $N_{\rm p_z}$ while the rise of O_{p_x} PDOS for the occupied energy region indicates the occurrence of charge transfer and reflection phenomena at the OH group.

S3 Local currents of the Gly homo-peptide

(NH)_i configurations. As discussed in the main text, the bond current analysis shows that the main contributions to the current in the case of the NH groups in the gap comes from the lower side chain and α -carbon, SC₁ and SC for, respectively, PB_1 and PB_2 . The lower residue is in the range [0.82 Å - 1.05 Å] below the GNR plane and this circumstance favors the overlap of both the π and π^* orbitals with the ones of the residue. This finding is consistent with the PDOS analysis of Fig. 4 of the main text showing the major contribution from the "lower" α -carbon and side chain. We see from Table S1 that the electron injection at the left lead proceed also, but at a largely minor extent, through both the "upper" side chain and the PB too; however, while the first one contributes to the electron transfer to the right, the PB role is more complex: the NH group may also contribute to the current (see the case of PB_2 where the N_{p_z} PDOS is more pronounced above the Fermi energy) while the CO group acts as a reflector at the right lead. i.e. electrons are injected into the PB from the left lead also trough the CO group (but at a small extent), and are reflected back to the CO group itself from the right lead. It is interesting to note the reflection occurring at both the $(CO)_i$ groups of the two PBs in the configuration $(NH)_2$. In any case, we see that the PB contribution from the NH group is much smaller than the one from the lower residue. It is also worth noticing that the NH role in the current transfer phenomena is

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Fig. S1 Transmission function of the hydrated ZGNR as compared to the dry one (a) and of the optimized configuration of a ZGNR nano-gap with a water molecule in between as compared to the one corresponding to the minimum current value measured in the Gly homo-peptide (b). The atomistic models of these optimized configurations are shown in the insets.



Fig. S2 PDOS decomposition in the atomic orbital basis for the four current maxima measured in the three Gly peptide. The cases with the *NH* and *CO* bonds in the middle of the nano-gap for the two PBs are respectively on the left and on the right.

also consistent with the PDOS analysis of Fig. S2 where it is shown that the major contribution to the PDOS from the PB comes exactly from the N_{pz} orbital. Therefore some overlap is possible between the N_{pz} orbital, that is slightly off the GNR plane, and both the π and the π^* orbitals of respectively the left and the right GNR leads (see the *PB*₂ case). In summary electron injection occurs from the left lead mainly through the lower residue and only at a minor extent through the PB; then, charge transfer phenomena between the various atomic groups are such that the electrons are transferred to the right lead mainly via the lower side chain and, at a minor extent, via the upper side chain. The NH group might contribute also. The *CO* group acts as reflection site especially at the right lead.

 $(CO)_i$ configurations. As discussed in the main text, the local current analysis in this case, measured for both PB_1 and PB_2 , evidences that the electron are injected from the left lead mainly through both the "upper" α -carbon and side chain, i.e. the closest to the CO group at the N-terminal side of the Gly homo-peptide, and through the NH group of the same PB at almost the same extent as the upper residue. The upper residues SC and SC₂ of, respectively, PB_1 and PB_2 are within the range [0.95 - 1.31] above the GNR plane, thus a bit more distant from the GNR plane than the "lower" residue in the case of the *NH* group in the gap. Nevertherless we see that the side chain contribution to the current is nearly the same for the two peaks within a given PB, even though they come from the "lower" or the "upper" residue. However, what makes the difference between the two peaks in a given PB signal is the contribution to the injection from the NH group that is rather small in the case of the first peak (with the NH group in the gap) while is almost of the same magnitude as the side chain one in the case of the second peak. This is mainly due to the off-plane position of the NH group in this second case (the NH groups are in the range [1.05 Å - 1.43 Å] below the GNR plane) that favors the overlap between the N_{p_z} orbital and both the π and the π^* orbitals of the leads. We see also a small contribution to the injection of electrons from the left lead through the second nearest residue, SC_1 and SC for respectively PB_1 and PB_2 . Lastly, we notice that the CO group behaves as a reflection site for the electrons injected both from the left and to the right leads in a pronounced way; this because the CO group is approximately in the GNR plane and, therefore, both the C_{pz} and the O_{p_z} orbitals of the CO partial bond have a little overlap with the π and the π^* GNR orbitals. Charge redistribution after the injection from the left lead is particularly pronounced especially concerning the NH group: indeed we see that the electrons are just partially transferred from the NH group to the right lead while the current is more concentrated in the upper side chain at the right lead side: indeed we see that the the local current at the upper side chain is almost doubled at the right lead with respect to the left lead for $(CO)_2$ while it is increased by nearly 50% for $(CO)_1$.

Table S1 Main local current contributions to the whole current flowing from the right to the left lead through the two Gly-Gly PBs analyzed.

		local current	local current
configuration	atomic group	from the right lead	into the left lead
		(nA)	(nA)
(<i>NH</i>) ₁	SC_1	1.027	0.67
	$(NH)_1$	0.0	0.045
	$(CO)_1$	-0.092	0.034
	SC	0.157	0.055
(<i>CO</i>) ₁	SC_1	0.125	0.139
	$(NH)_1$	0.238	0.44
	$(CO)_1$	-0.052	-0.085
	SC	0.972	0.63
	$(NH)_2$	0.009	0.007
(<i>NH</i>) ₂	$(CO)_1$	-0.199	-0.154
	SC	1.036	0.857
	$(NH)_2$	0.155	0.152
	$(CO)_2$	-0.077	0.032
	SC_2	0.175	0.071
(<i>CO</i>) ₂	SC	0.205	0.218
	$(NH)_2$	0.205	0.529
	$(CO)_2$	-0.117	-0.055
	SC_2	1.457	0.773

The PB double bond behavior. As extensively discussed in the main text, we see from the data of Table S1 that the main reason why the second peak of the PB fingerprint is larger than the first one resides in the larger contribution from the NH group of the PB itself. This is most probably due to the nature of the PB where the CO double bond is, actually, partial with the double bond that resonates between CO (60 %) and CN (40 %). This causes the well known PB bond stiffness for rotations around the CN. The double bond resonance, indeed, involves the C_{p_z} and O_{p_z} orbitals, each one filled with one electron, and the N_{p_z} lone pair so that the oxygen and the nitrogen atoms are, respectively, negatively and positively charged. As a consequence, the N_{p_z} orbital is not fully occupied and can participate to the electron transfer through the peptide. More interestingly, we see that when the $N_{p_{\tau}}$ orbital overlaps to the π and π^* GNR orbitals of the left and the right GNRs leads, i.e. when the N_{pz} orbital is just above or below the GNR plane, it can be easily considered to be delocalized on the π and π^* GNR orbitals thus favoring the electron transfer across the PB. The electron reflection occurring at the CO group, that is particularly pronounced in the $(CO)_i$ case, is caused by both the negative charge transfer at the oxygen atom (and the presence of the two O lone pairs) and the fact that the C_{p_z} orbital is fully involved in the resonant double bond between CO and CN.

The (SC) configuration. In this configuration the electrons are injected from the left lead mainly through the closest $(NH)_2$ group, that, however, does not show the largest PDOS

Table S2 Main bond current contributions to the whole current flowing from the right to the left lead through the Gly residue.

		bond current	bond current
configuration	atomic group	from the right lead	into the left lead
		(nA)	(nA)
SC	SC_1	0.037	0.015
	$(NH)_1$	0.083	0.114
	$(CO)_1$	0.051	0.090
	SC	-0.038	-0.044
	$(NH)_2$	0.096	0.146
	$(CO)_2$	0.068	0.0

(see Fig.6(a) in the main text), and through $(CO)_1$ and $(NH)_1$ of PB_1 at nearly the same extent. Contrarily to the configurations of two current peaks, in this case the central side chain SC behaves as a reflecting group both for electron injection from the left lead into the peptide and from the peptide into the right lead because the overlap with π and π^* is poor. After the electron injection from the left lead, the charge redistributes across the two PBs and the current flows to the right lead though both the CO and the NH groups of the two PBs, with a major role of the NH groups. In any case, the Gly residue does not participate to the current transfer. Hence the measured signal is a fingerprint of the two PB involved, with a prominent role of the "upper" $(NH)_2$ group that is the main injection point for the electrons. It is worth to emphasize that the total current measured at this point has nearly the same level as the bond current flowing across the NH group for the second peaks (with the CO groups in the middle of the gap). This circumstance suggests that PBs have a specific fingerprint in terms of the transverse current: this is basically due to the overlap between the p_z orbitals, involved in the PBs resonant double bond, and the π and the π^* GNR orbitals and causes, at the same extent, the difference between the two peaks (obtained with NH and CO in the gap) and the minimum current value measured with the Gly residue in the gap. We can explain such behavior by observing that the best overlap between the partially occupied $N_{\text{p}_{z}}$ orbital and both the π and the π^* GNR orbitals occurs with the *CO* group in the middle of the gap (the second peak of the PB current signal): in this case the current injection through the PB (i.e. through the NH group) is maximum. On the contrary such an overlap is minimized for configurations with the NH group in the gap and nearly no injection through the PB occurs. In the case of the Gly side chain in the gap, we have a partial overlap of π and π^* with both the upper and the lower resonant double bonds of respectively PB_1 and PB_2 with a major role played by the *NH* groups. Because in this case no injection occurs through the side chain and the α -carbon, the minimum current signal reflects the PB ability to link directly the left lead HOMO and the right lead LUMO orbitals with no role from the residues.