Journal Name

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Supplementary Information: Enhanced thermopower in covalent graphite-molecule contacts

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S1 Transmission function for model molecular junctions

We derive here the Eqs. (4) and (6) in the paper, which express the transmission function for a molecule with a single orbital of energy E_0 coupled to a bottom and a top electrode.
By using the Green's function formalism, the transmission function reads

$$\tau(E) = \mathrm{Tr}\left[\Gamma_B(E) G^{\dagger}(E) \Gamma_T(E) G(E)\right]. \tag{S1}$$

$G(E)$ is the Green's function of the molecule

$$G(E) = \frac{1}{E - E_0 - \Sigma_B(E) - \Sigma_T(E)}, \tag{S2}$$

with the complex self-energy $\Sigma_{B(T)}(E)$, which accounts for the contact with the bottom (top) electrode. The electronic coupling function $\Gamma_{B(T)}(E)$ is then defined as

$$\Gamma_{B(T)}(E) = i[\Sigma_{B(T)}(E) - \Sigma^{\dagger}_{B(T)}(E)]. \tag{S3}$$

Assuming that the real parts of the self-energies are zero, we have $\mathrm{Im}\Sigma_{B(T)}(E) = -\Gamma_{B(T)}(E)/2$ and the Green's function becomes

$$G(E) = \frac{1}{E - E_0 + \frac{i}{2}[\Gamma_B(E) + \Gamma_T(E)]}. \tag{S4}$$

The transmission function calculated by inserting $G(E)$ into Eq. (S1) then reads

$$\tau(E) = \frac{\Gamma_B(E)\Gamma_T(E)}{(E - E_0)^2 + \frac{1}{4}[\Gamma_B(E) + \Gamma_T(E)]^2}. \tag{S5}$$

This is a general expression for a single molecular orbital in between two electrodes. Next we consider two cases: 1) both electrodes are equal and made of gold, 2) the top electrode is made of gold, while the bottom electrode is made of graphene or graphite. In the first case we can assume that the coupling functions of the two electrodes are energy independent and we set $\Gamma_B(E) = \Gamma_T(E) = \Gamma/2$. Hence the transmission is

$$\tau(E) = \frac{1}{4}\frac{\Gamma^2}{(E - E_0)^2 + \frac{1}{4}\Gamma^2}, \tag{S6}$$

which is Eq. (4) in the paper.
In the second case, we set $\Gamma_T(E) = \Gamma/2$ and $\Gamma_B(E) = \Gamma_0|E|$. We then have that

$$\tau(E) = \frac{1}{2}\frac{\Gamma\Gamma_0|E|}{(E - E_0)^2 + \frac{1}{4}(\Gamma/2 + \Gamma_0|E|)^2}, \tag{S7}$$

which is Eq. (6) in the paper.

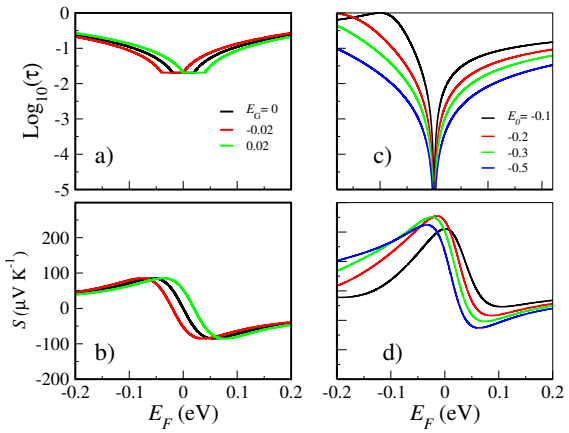

Fig. S1 a) Transmission function for model graphene, where the Dirac-like cone around the CNP has been smeared into a 40 meV-wide plateau. This transmission function qualitatively resembles the one of the graphite/PPD/Au junction. E_G (given in eV) is the energy shift of the transmission function induced by gating. b) Corresponding thermopower. c) Transmission function for a model of a molecule with one orbital of energy E_0 (in eV) attached to two graphene electrodes. d) Corresponding thermopower. Note that the transmission functions are plotted in logarithmic scale like in Fig. 1 of the paper.

S2 Other models for molecular junctions

We present here the transmission and thermopower for two models, which complete the overview presented in Sec. 2 of the paper.

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S2.1 Model for the graphite/PPD/Au junction

The graphite/PPD/Au junction presents a transmission function with a broadened minimum (see Fig. 3-c in the paper). Therefore we modify our model for graphene in such a way that the transmission function $\tau(E)$ has a 40 meV plateau instead of a Dirac-like charge neutrality point (CNP). This is shown in Fig. S1-a for different gate voltages E_g, which shift in energy the center of the plateau. The thermopower S as a function of E_F at 300 K is plotted in Fig. S1-b. After comparing Fig. S1-b here to Fig. 1-d in the paper, the main conclusion is that the presence of the plateau instead of the CNP does not have any visible effect on the S vs E_F curves at 300 K (see below for a discussion about different temperatures).

S2.2 Model for a junction with two graphene electrodes

We examine here a model for a molecule with one orbital of energy E_0 attached to two graphene electrodes. The transmission can be readily calculated by using Eq. (S5) with $\Gamma_T(E) = \Gamma_B(E) = \Gamma_0|E|$ and it is plotted in Fig. S1-c. The corresponding S as a function of E_F is then presented in Fig. S1-d. Both τ and S are qualitatively very similar to those presented in Fig. 3-g and 3-h of the paper, where only one C-based electrode was considered. Therefore we conclude that the same arguments used to predicted an enhanced thermopower in hybrid junctions can be readily extended to the study of fully graphene-based junctions.

S3 Temperature dependence of S

The results presented in the paper for graphite/PPD/Au and graphite/DMAB/Au were obtained at 300 K as experiments are often performed at this temperature. Here we extend our study to show how S depends on the temperature. Before considering the real junctions studied from first-principles, it is useful to examine some of our models to better understand the general qualitative features that we should expect. All results in the following subsections are for $E_F = 0$ eV.

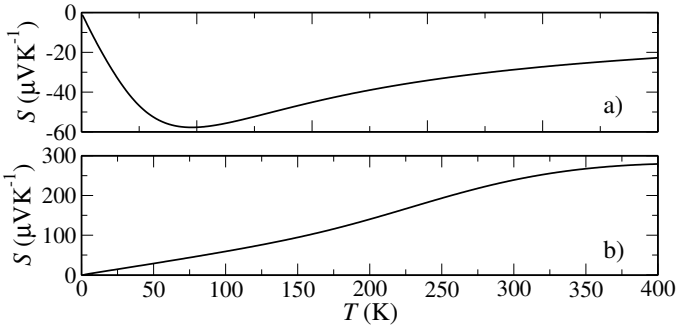

Fig. S2 Thermopower at $E_F = 0$ eV as a function of the temperature for the model describing a) graphite/PPD/Au and b) graphite/DMAB/Au.

S3.1 Model results

The transmission $\tau(E)$ of graphite/PPD/Au is modelled as described in Sec. S2.1 and in Fig. S1-a. We set $E_G = -0.02$ eV so that the Fermi energy is at the right edge of the plateau region similarly to what found in the results of the first-principles calculations of Fig. 3-a in the paper. It is this gating, which makes $\tau(E)$ asymmetric with respect to E_F, leading to a finite S and mimicking the effect of the molecule-graphite charge transfer described Sec. 3.2 in the paper. S is plotted as a function of the temperature T in Fig. S2-a. S is negative over the whole considered temperature range. In particular, at low temperatures S is found to vary linearly with T according to the low energy expansion [1]

$$S = \frac{\pi^2 k_B^2 T}{3e} \frac{\partial \ln \tau(E)}{\partial E}\bigg|_{E=E_F}. \tag{S8}$$

Next, there is an intermediate temperature range, where the absolute value of S reaches a maximum value. Finally, at higher temperatures, $|S|$ decreases monotonically as a function of T until it starts saturating towards an asymptotic value. These qualitative observations can be easily understood by remembering that the thermopower is calculated by performing an integration over the energy [see Eq. (2) in the paper]. The integration region is determined by the width of the derivative of the Fermi function $f' = \partial f/\partial E$, which is plotted in Fig. S3. At intermediate temperatures (such as 80 K) the transmission function inside the integration region is constant for $E - E_F < 0$, while it depends linearly on E for $E - E_F > 0$. $\tau(E)$ is therefore very asymmetric with respect to E_F and, as a results, we find the largest absolute value of the thermopower. Conversely, S is reduced for higher temperatures, when both the extension in energy of the plateau region and the gate-induced energy shift of the transmission are negligible with respect to the integration energy interval.

The transmission of graphite/DMAB/Au is modelled according to Eq. (S7) (Fig. 1-g in the paper) with $E_F = 0$ eV, which coincides with the charge neutrality point. S as a function of T is plotted in Fig. S2-a. In contrast to the previous case, S is here always positive and increases monotonically with the temperature until it eventually saturates to a large value. This difference is due to the fact that in this model the transmission function has a different energy dispersion for positive and negative energies, while in the previous model $\tau(E)$ was made asymmetric with respect to $E_F = 0$ eV through a small gate potential.

S3.2 First-principles results

We now turn to the results of first-principles calculations. The thermopower is obtained by using the transmission function in Fig. 3-c and 3-e of the paper for graphite/PPD/Au and graphite/DMAB/Au respectively. The results are reported in Fig. S4. We note that there is a general qualitative agreement between the first-principles results and those of the models just discussed (we remind that no quantitative agreement is expected as the parameters used in the models are arbitrary and not fitted to the first-principles results).

The thermopower as a function of T for the graphite/PPD/Au junction in presented in Fig. S4-a. It remains negative over a wide temperature range. Like in the model, $|S|$ reaches a local

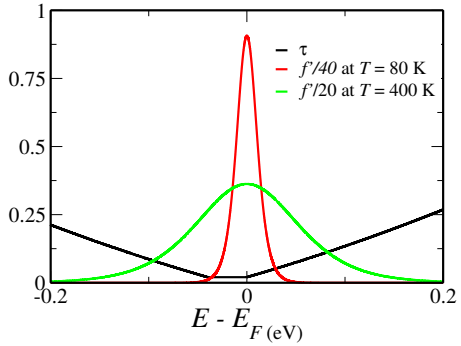

Fig. S3 Black line: same transmission function (in linear scale) as in Fig. S1-a for $E_G = -0.02$ eV. Red line: derivative of the Fermi function $f' = \partial f/\partial E$ (divided by 40 for better display) at $T = 80$ K. Green line: derivative of the Fermi function $f' = \partial f/\partial E$ (divided by 20 for better display) at $T = 400$ K.

maximum before decreasing monotonically. In particular, this local maximum is found to be between 170 K and 190 K depending on the graphite-molecule angle.

The thermopower as a function of T for the graphite/DMAB/Au junction is presented in Fig. S4-b. S is positive for $T >\sim 50$ K and it grows monotonically with the temperature until it eventually saturates to $S \approx 120\ \mu V K^{-1}$ near room temperature. S is instead negative at $T <\sim 50$ K. However, this may be an artefact due to the noise of the transmission function. In fact $\tau(E)$ has a lot of tiny asymmetric features due, for example, to the finite k-points sampling. These tiny features affect S at low temperature when their energies are comparable to the width of f'. In contrast, for $T >\sim 50$ K they become irrelevant with respect to the general shape of $\tau(E)$.

In summary, for temperatures around 150 K graphite/PPD/Au and graphite/DMAB/Au have similarly large thermopowers, but of opposite sign. Graphite/DMAB/Au remains by far the best performing junction for any temperature above 150 K.

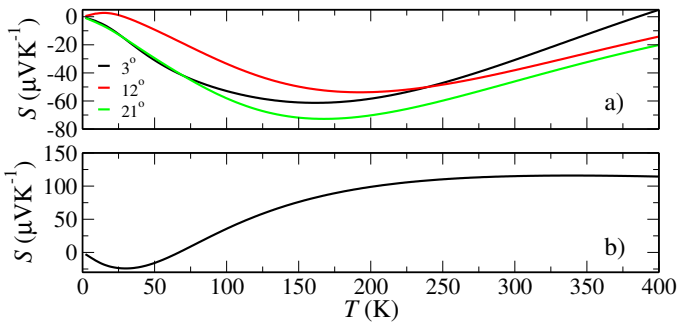

Fig. S4 Thermopower at $E_F = 0$ eV as a function of the temperature for a) graphite/PPD/Au and b) graphite/DMAB/Au.

S4 Electronic thermal conductance and figure of merit

The moment of order n of the transmission function $\tau(E)$ is defined as

$$L_n = \int_{-\infty}^{\infty} dE (E - E_F)^n \tau(E) \Big[-\frac{\partial f(E)}{\partial E} \Big]. \quad \text{(S9)}$$

As discussed in paper, the conductance and the thermopower are respectively proportional to the moment of order 0 and 1, while the calculation of the thermal conductance G_{th} requires also the moment of order 2. In fact we have that[2]

$$G_{th} = \frac{1}{hT} \Big(L_2 - \frac{L_1^2}{L_0} \Big). \quad \text{(S10)}$$

with h the Planck's constant.

The figure of merit ZT can be expressed as

$$ZT = \frac{1}{\frac{L_0 L_2}{L_1^2} - 1}. \quad \text{(S11)}$$

This is the equation that was used to compute ZT in Sec. 3.3. of the paper.

Notes and references

1 Y. Dubi and M. Di Ventra, *Rev. Mod. Phys.*, 2011, **83**, 131.

2 C. M. Finch, V. M. Garcia-Suarez and C. J. Lambert, *Phys. Rev B*, 2009, **79**, 033405.