

Supporting Material: Permeation of chemisorbed hydrogen through graphene: a flipping mechanism elucidated

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TABLE S1: Formation enthalpy (ΔH_f) for the addition of n hydrogen atoms on a graphenic ring (see Eq. 1 in the main manuscript) as well as activation (ΔH_a) and reaction (ΔH_r) enthalpies for the flipping process as estimated by using the PBE, B3LYP and M062X functionals together with the cc-pVTZ basis sets. The $n=4,5$ arrangements (see Fig. 1 in the main manuscript) of chemisorbed hydrogen atoms have been considered. All values are in eV.

| | | H atoms addition | | |
|--------------|-----|------------------|--------|--------|
| | | PBE | B3LYP | M062X |
| ΔH_f | n=4 | -5.671 | -5.639 | -5.965 |
| | n=5 | -6.298 | -6.302 | -6.579 |
| | | flipping | | |
| | | PBE | B3LYP | M062X |
| ΔH_a | n=4 | 2.670 | 2.903 | 3.366 |
| | n=5 | 1.580 | 1.662 | 1.897 |
| ΔH_r | n=4 | -0.500 | -0.541 | -0.588 |
| | n=5 | -0.730 | -0.747 | -0.811 |

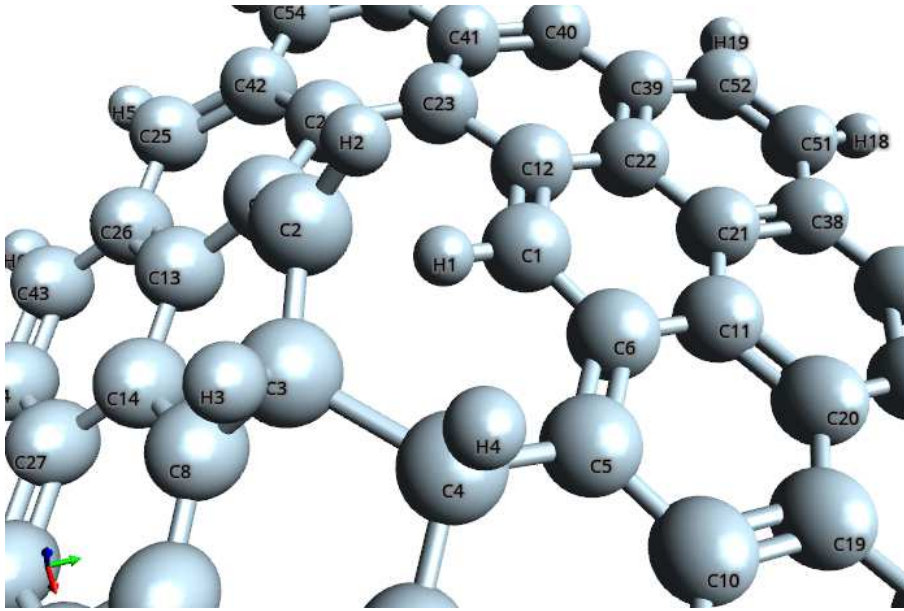


TABLE S2: CM5 charges (in a.u.) of the four hydrogen atoms chemisorbed along the central ring of the $n = 4$ arrangement (see Fig. 1) of hydrogenated circumcoronene, together with those of the carbon atoms linked to them, for the reactant and flipping transition states and for different charge dopings, $q = -2, 0$ and 2 a.u., corresponding to electron doping, no doping and hole doping, respectively. Σ_H and Σ_C are the sums of the charges of these four H and C atoms, respectively, and $\Sigma_{H,C}$ is the total sum. Labeling of the considered atoms corresponds to that in the image shown above, where the geometry of the transition state of the neutral prototype is depicted.

| | Reactants | | | Transition State | | |
|----------------|-----------|---------|----------|------------------|---------|----------|
| | $q = -2$ | $q = 0$ | $q = +2$ | $q = -2$ | $q = 0$ | $q = +2$ |
| H1 | 0.097 | 0.115 | 0.136 | 0.099 | 0.111 | 0.120 |
| H2 | 0.096 | 0.109 | 0.122 | 0.091 | 0.116 | 0.145 |
| H3 | 0.096 | 0.109 | 0.122 | 0.090 | 0.113 | 0.139 |
| H4 | 0.097 | 0.115 | 0.136 | 0.084 | 0.115 | 0.132 |
| Σ_H | 0.386 | 0.448 | 0.516 | 0.364 | 0.455 | 0.536 |
| C1 | -0.070 | -0.065 | -0.057 | -0.111 | -0.102 | -0.062 |
| C2 | -0.070 | -0.066 | -0.061 | -0.116 | -0.088 | -0.025 |
| C3 | -0.070 | -0.066 | -0.061 | -0.075 | -0.066 | -0.055 |
| C4 | -0.070 | -0.065 | -0.057 | -0.068 | -0.056 | -0.042 |
| Σ_C | -0.280 | -0.262 | -0.236 | -0.370 | -0.312 | -0.184 |
| $\Sigma_{H,C}$ | 0.106 | 0.186 | 0.280 | -0.006 | 0.143 | 0.352 |

TABLE S3: Doping dependence of the activation (ΔE_a) and reaction (ΔE_r) energy for the hydrogen flipping, diffusion, desorption and recombination processes which can occur starting from the $n=4$ arrangement (see also Fig. 1). Notice that for the desorption process the same value as for ΔE_r is assumed for ΔE_a since no transition state has been found for this process. All values are in eV.

| n=4 | doping | flipping | diff. | desorpt. | recomb. |
|--------------|----------|----------|-------|----------|---------|
| ΔE_a | neutral | 2.79 | 1.94 | 2.27 | 2.10 |
| | hole | 1.79 | 0.89 | 1.54 | 2.28 |
| | electron | 1.71 | 1.68 | 1.44 | 1.92 |
| ΔE_r | neutral | -0.51 | 1.90 | 2.27 | -0.82 |
| | hole | -0.46 | 0.37 | 1.54 | -1.19 |
| | electron | -0.59 | 0.58 | 1.44 | -1.12 |

TABLE S4: Isotopic dependence of the activation (ΔH_a) and reaction (ΔH_r) enthalpies for the flipping and recombination processes. For the flipping the $n=4,5$ initial arrangements of chemisorbed atoms (hydrogen or deuterium) have been considered while recombination refers to the $n=2$ case and occurring for both para and ortho mechanisms (see also Table 3 in the main manuscript). All values are in eV.

| | | flipping | |
|--------------|-------------|---------------|-----------|
| | | hydrogen | deuterium |
| ΔH_a | n=4 | 2.670 | 2.681 |
| | n=5 | 1.580 | 1.592 |
| ΔH_r | n=4 | -0.500 | -0.495 |
| | n=5 | -0.730 | -0.724 |
| | | recombination | |
| | | hydrogen | deuterium |
| ΔH_a | n=2 (para) | 1.024 | 1.088 |
| ΔH_a | n=2 (ortho) | 2.415 | 2.515 |
| ΔH_r | n=2 (para) | -1.855 | -1.765 |
| ΔH_r | n=2 (ortho) | -1.904 | -1.804 |

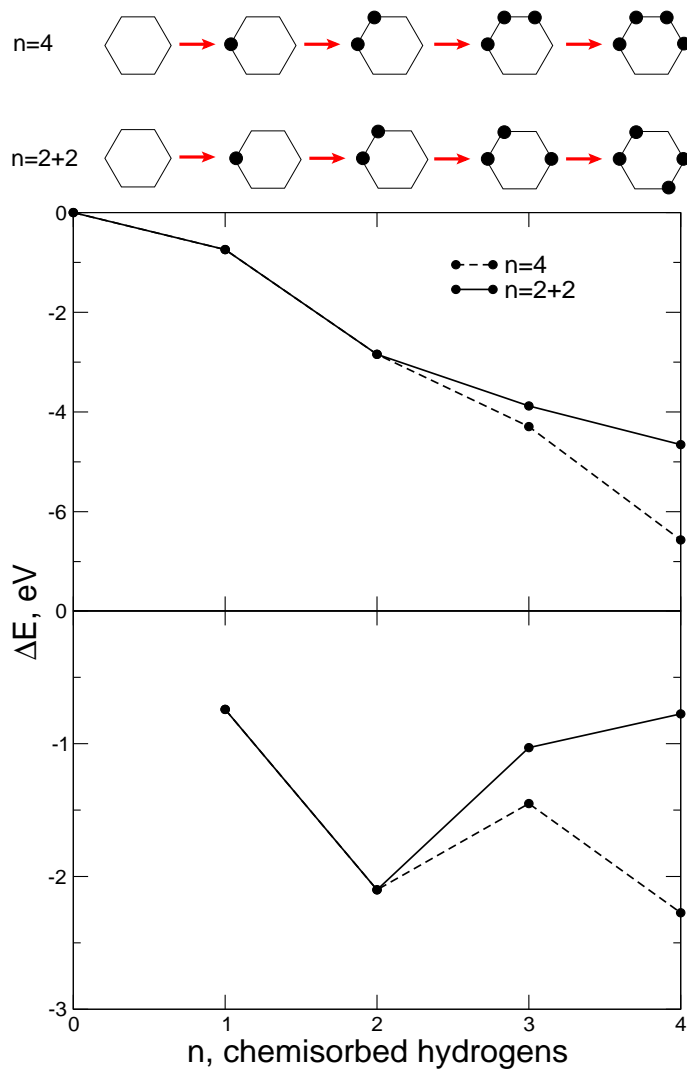


FIG. S1: Possible hydrogenation paths for the $n=4$ and $n=2+2$ arrangements on a graphenic ring. Upper panel: electronic energy variation (ΔE) corresponding to the addition of n hydrogen atoms, with respect to the unsaturated graphene molecular prototype ($n=0$) and n isolated hydrogen atoms. Lower panel: electronic energy variation (ΔE) at each hydrogenation step ($(n-1) \rightarrow (n)$, $n=1-4$).

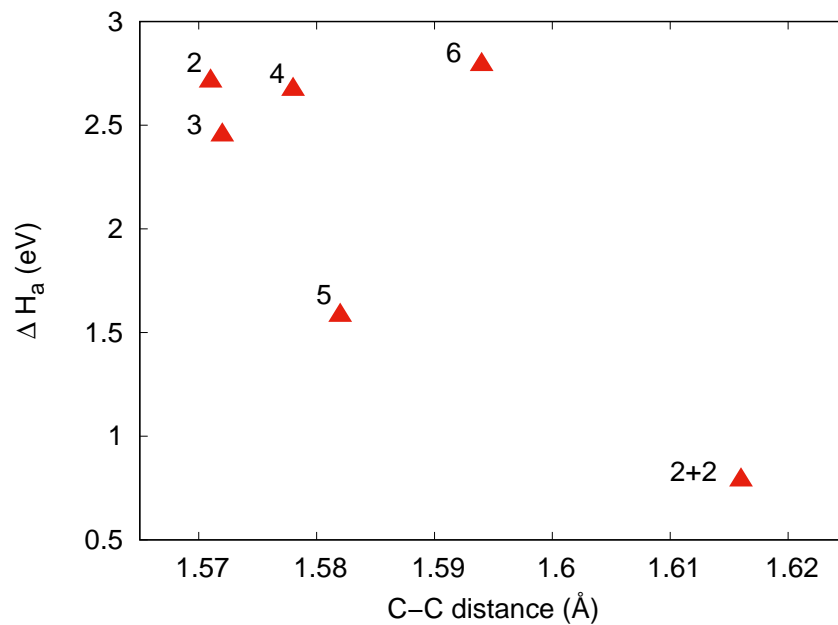


FIG. S2: Activation enthalpy ΔH_a for the flipping of one hydrogen atom as a function of the length, in the initial chemisorbed state, of the C-C bond that breaks in the transition state (see also Fig. 2). The considered bond lengths correspond to the $n=2-6$ and $2+2$ initial states and the reported data refer to the circumcoronene prototype.