Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Electrostatic Patterning on Graphene with Dipolar Self-Assembly

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Ab initio molecular dynamics (AIMD) simulations were performed to verify the dynamical stability of the μ-Up and μ-Down networks. We have followed a similar procedure than previous works investigating the stability of stacked heterostructures and self-assembled systems.[1–4] The simulations were performed over 5 ps at 250 K on "super-flower" configuration which represents the more thermodynamically stable structure at this temperature. The temperature was controlled through a Nosé thermostat[5] implemented in SIESTA. The total energy profiles obtained from AIMD are shown in Figure S1. Both systems give rise to total energy fluctuation that is about thermal energy ($\sim$20 meV) which is negligible with respect to the total energy, or even adsorption energies of the systems. In addition, no bond breaking nor structural transitions were observed along the simulations. AIMD results support the dynamically stability of the systems considered here.

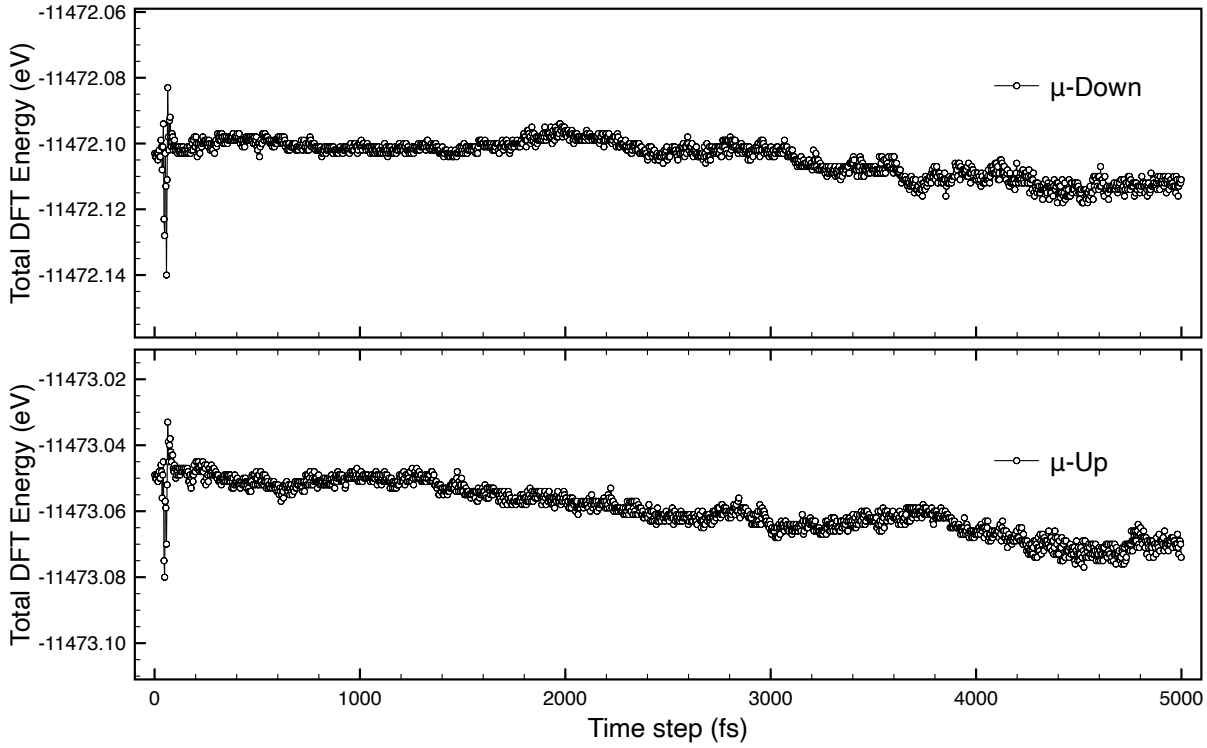

Figure S1: Variation of total energy within AIMD simulation over 5 ps on μ-Down (upper panel) and $\mu - Up$ (lower panel) SAN networks.Time step = 1 fs, T = 250 K.

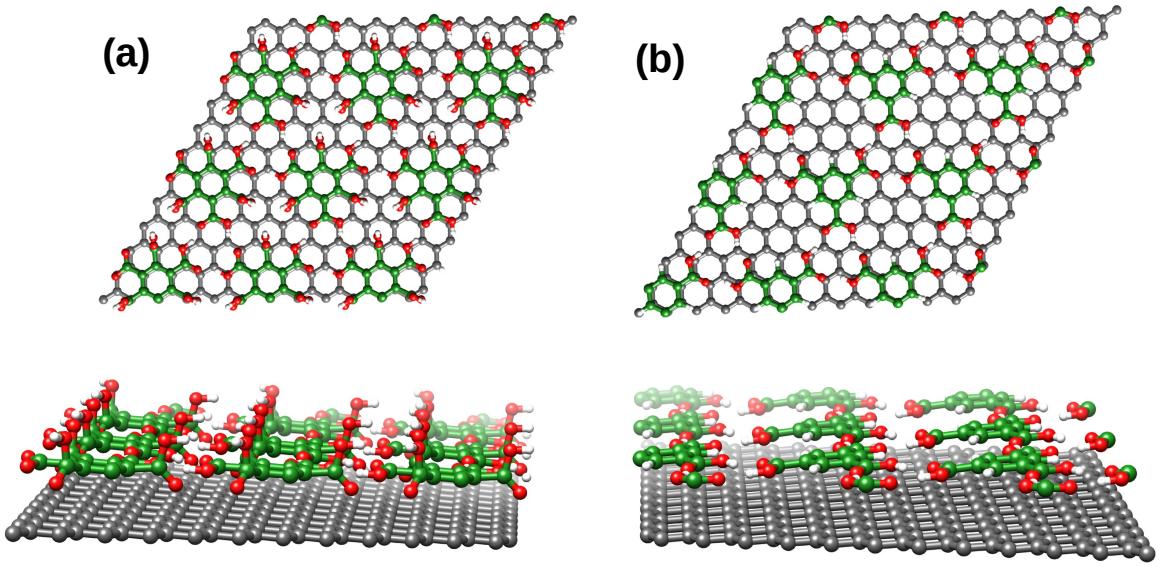

Figure S2: Top and side views of a 3×3 model for functionalized TMA (a) -COOH and (b) -H. For better contrast, the C atoms are displayed in gray for graphene and in green for the molecular units, otherwise H, O atoms are displayed in white and red, respectively. The unit cells contain 32 Carbon atoms for the graphene substrate, 30 atoms (12C, 12O, 6H) for (a) -COOH and 21 atoms (9C, 6O, 6H) for (b) -H.

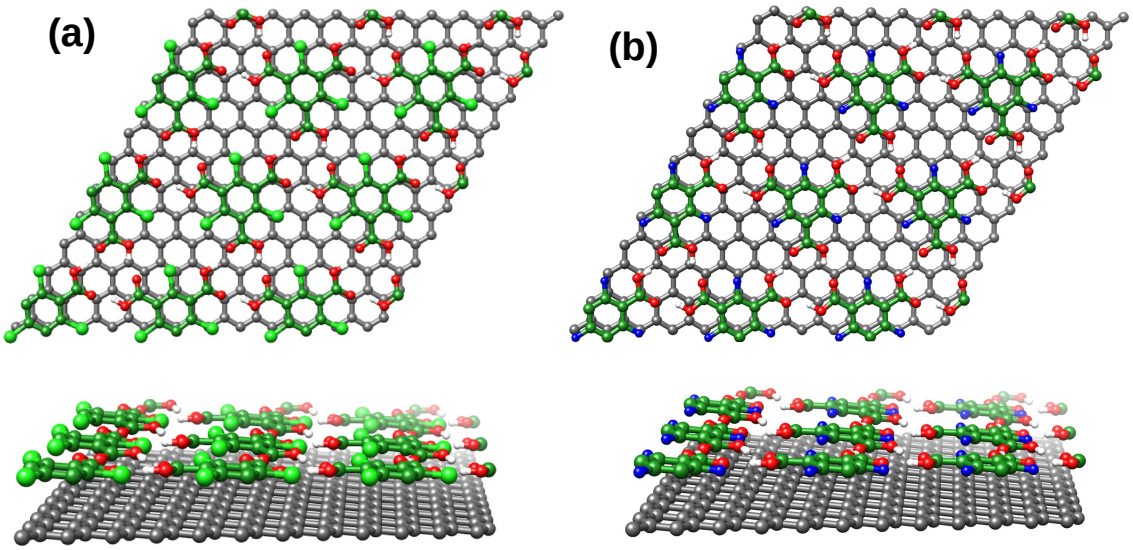

Figure S3: Top and side views of a 3×3 model for functionalized TMA on graphene (a) -Cl (b) -F. C atoms of graphene are gray, C atoms of molecules are green, and H, O, Cl, F atoms are in white, red, light green and blue, respectively. The unit cells contain 32 Carbon atoms for the graphene substrate, 21 atoms (9C, 6O, 3H, 3Cl) for (a) -Cl and 21 atoms (9C, 6O, 3H, 3F) for (a) -F.

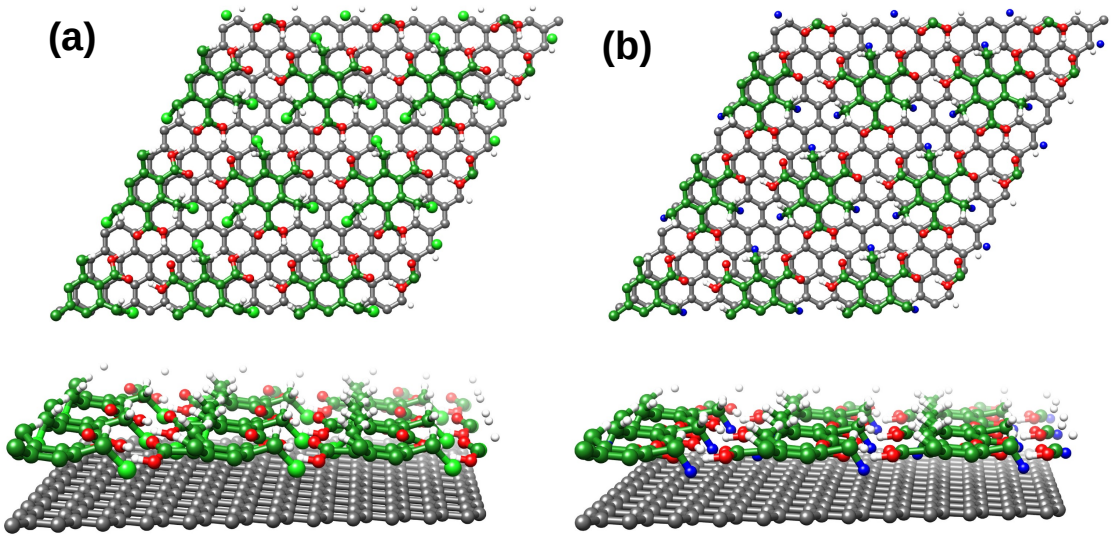

Figure S4: Top and side views of a 3×3 model for functionalized TMA on graphene (a) -CH_2Cl (b) -CH_2F. C atoms of graphene are gray, C atoms of molecules are green, and H, O, Cl, F atoms are in white, red, light green and blue, respectively. The unit cells contain 32 Carbon atoms for the graphene substrate, 30 atoms (12C, 6O, 9H, 3Cl) for (a) -Cl and 30 atoms (12C, 6O, 9H, 3F) for (b) -F.

The presence of the functional groups on the geometry of the SAN mostly influences the height of the networks over the graphene substrate. The average height of the different optimized SAN are reported in Table S1. For simplicity, we averaged the heights of the more central Carbon atoms of the TMA benzene ring. The variations of height reflect the relative position of the functional groups where larger variations are observed when they are pointing toward the graphene substrate.

Table S1: The influence of the functional groups in TMA on their relative height h (in Å) over graphene.

molecular units	h (Å)
-H	3.17
-F	3.17
-Cl	3.21
-COOH	3.22
-OCH_3 μ-Up	3.17
-OCH_3 μ-Down	3.41
-CH_2F	3.31
-CH_2Cl	3.52

References

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