Supporting information

Characterizing self-assembled molecular layers on weakly interacting substrates: the role of the van der Waals and the chemical interactions

Lucía Rodrigo,[1] Pablo Pou,[1, 2] Ruth Martínez-Casado,[1,3,4] Antonio J. Martínez-Galera,[5] José M. Gómez-Rodríguez,[5] and Rubén Pérez[1, 2]

[1]Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, ES-28049 Madrid, Spain

[2]Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, ES-28049 Madrid, Spain

[3]Univ Turin, Dipartimento Chim, IFM, I-10125 Turin, Italy

[4]C.R.F. S.C.p.A Strada Torino 50, I-10043 Orbassano (TO), Italy

[5]Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, ES-28049 Madrid, Spain

I. Experimentally determined moiré model for triazine/HOPG

By means of STM images as the one shown in Figure 9b) in the manuscript we have observed that, for the case of triazine on HOPG, the molecular array has a periodicity of around 6.1 Å and it is rotated by approximately 20º with respect to the atomic periodicity of the HOPG lattice. Our STM images also reveal that the superposition of molecular and HOPG lattices gives rise to a moiré-like superstructure with 40.3 Å periodicity. Based on this information about the geometry of the observed superstructure, we have developed a model which is presented in Figures S1 and S2. According to this model, the resulting superstructure is consistent with a $\left(2\sqrt{67}\times 2\sqrt{67}\right)-R12.2^{o}$ supercell, with respect to the HOPG substrate, with 43 molecules per unit cell. Therefore, the nominal coverage of this overlayer is 0.16 ML (referred to graphene). It is interesting to note that, consistent with our experimental observations, according to this model, the supercell would be rotated by 7.6º with respect to the molecular array, which would have exactly a periodicity of 6.14 Å and it would be rotated by 19.8º with respect to the lattice of the HOPG substrate. Likewise, a distance of 2.39 Å is extracted between a nitrogen atom of one molecule and a hydrogen atom of an adjacent molecule. It is consistent with the formation of C-H ⋯ N

hydrogen bonds between neighboring molecules. It should be mentioned that, for simplicity, only the outermost layer of the HOPG substrate has been drawn.

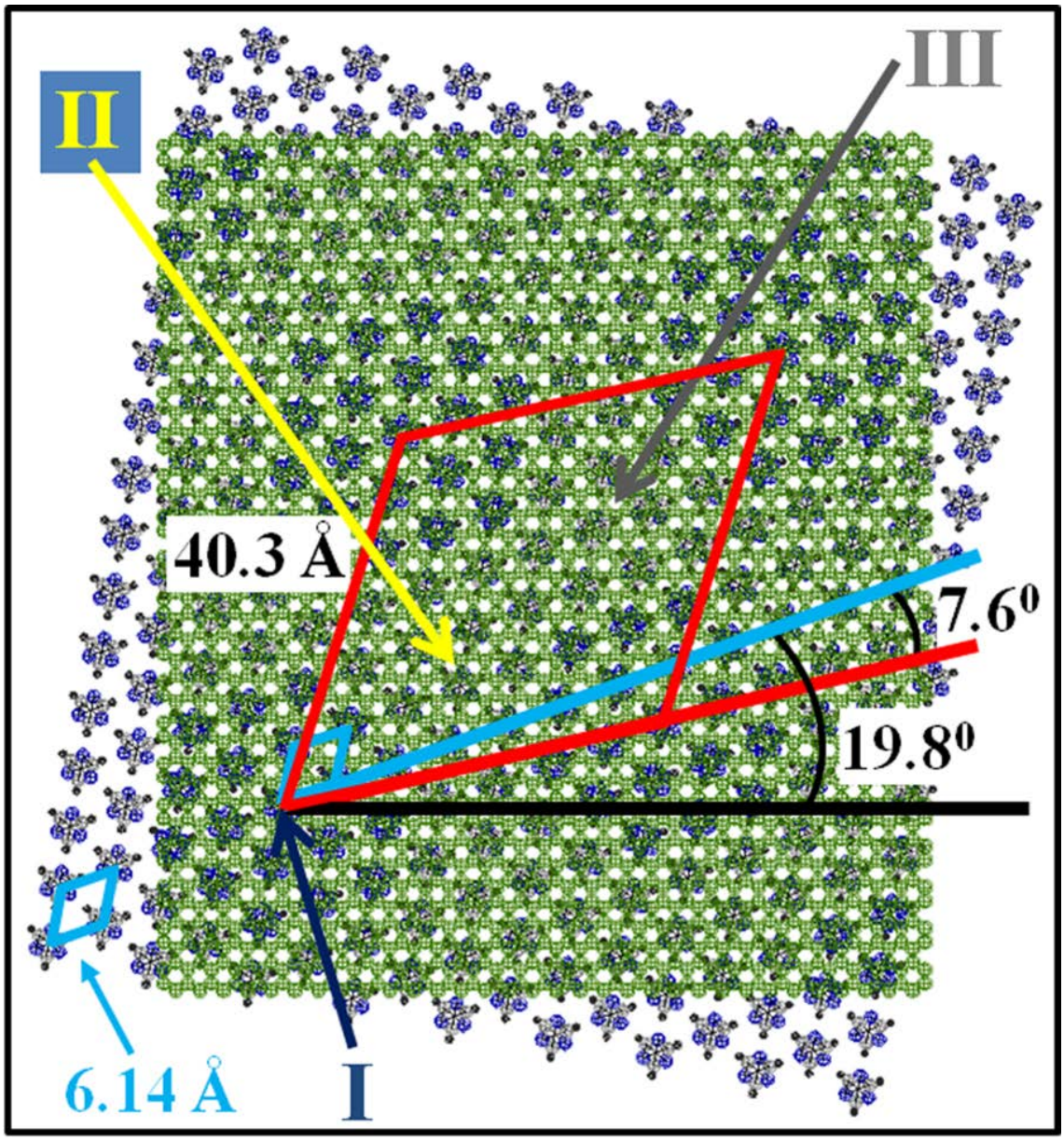

Figure S1. Schematic drawing for the proposed model for the adsorption of triazine on HOPG.

In order to facilitate the understanding of this model, we have divided the supercell in three different regions which are shown in Figure S2. In zone I there are 19 molecules, the molecule in the middle is centered on top of a carbon atom of the substrate on a C top configuration, and, as the other molecules are further away from it, their molecular rings are gradually deviated from the C top positions over carbon atoms belonging to the same sub-lattice. Zone II is composed of 12 molecules, the three ones in the center are placed close to N top positions over atoms of the other sub-lattice while, the remaining molecules

presents larger deviations from N top positions. Zone III consists of 12 molecules, the three ones around the midpoint are placed on an all top configuration, whereas the other molecules are deviated from these positions.

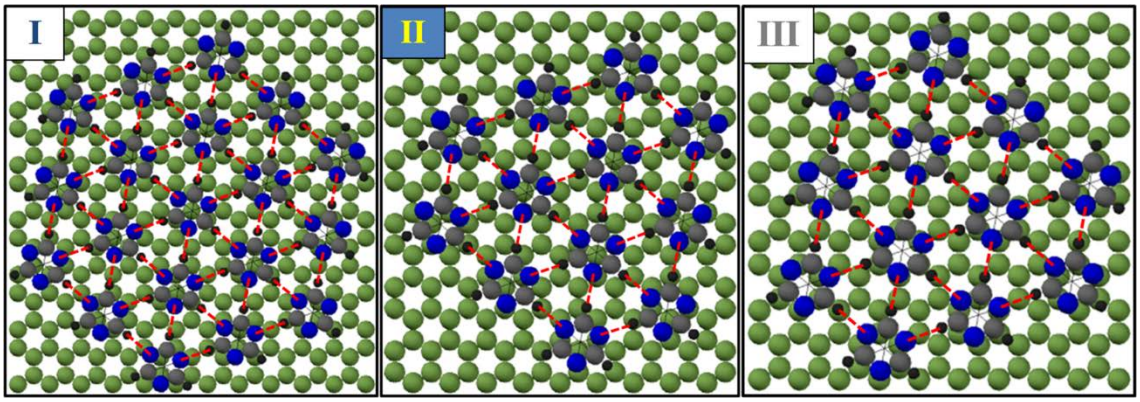

Figure S2. Zoom out of Zone I, II and III of the proposed model for the adsorption of triazine on HOPG. The red dashed lines indicate the formation of C-H ⋯ N hydrogen bonds between neighboring molecules.

II. Experimentally determined moiré model for triazine/graphene/Pt(111)

By means of STM images as the one shown in Figure 9c) in the manuscript we have observed that for the case of triazine on graphene/Pt(111) the molecular array has a periodicity of around 6.3 Å and it is rotated by approximately 21º with respect to the atomic periodicity of the graphene lattice. Our STM images also reveal that the superposition of molecular and graphene lattices gives rise to a moiré-like superstructure with 43.7 Å periodicity. According to these results we have developed a structural model consistent with a supercell with $\left(2\sqrt{79}\times 2\sqrt{79}\right)-R43^{o}$ periodicity with respect to the atomic lattice of the graphene surface (see Figure S3). According to this model the unit cell would have 49 molecules per unit cell. Then, it presents a nominal coverage of 0.155 ML. On the basis of this model a distance of 2.49 Å is extracted between a hydrogen atom of one molecule and a nitrogen atom of an adjacent molecule. This distance is consistent with the formation of C-H ⋯ N hydrogen bonds between neighboring molecules. Finally, it should be mentioned that, for simplicity, in this model it has only been considered the graphene layer without the Pt (111) substrate.

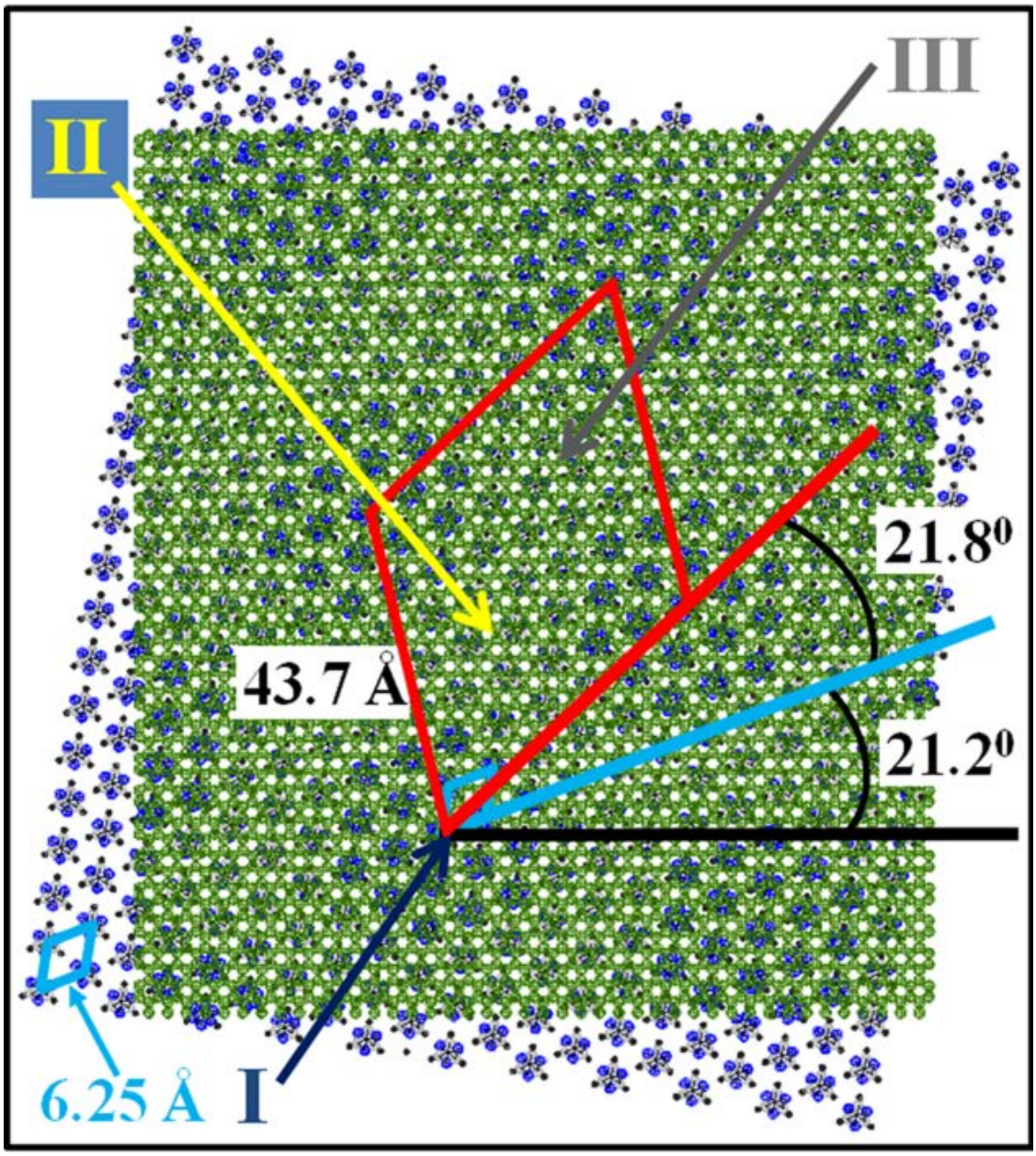

Figure S3. Schematic drawing for the proposed model for the adsorption of triazine on graphene/Pt(111).

In order to make easier the interpretation of this model the supercell has been divided into three different areas which are shown separately in Figure S4. In zone I there are 19 molecules, the one in the middle is centered on a C top position, while the molecular ring of the other molecules are progressively deviated from C top positions over carbon atoms in the same sub-lattice as they are farther from the molecule at the center. Zone II consists of 15 molecules, the three ones around the central point are placed close to N top positions with respect to the carbon atoms belonging to the other sub-lattice and the other molecules present larger deviations from N top positions. Zone III consists of 15 molecules, the three ones around the midpoint are located on all top positions whereas the other molecules present larger deviations from such positions.

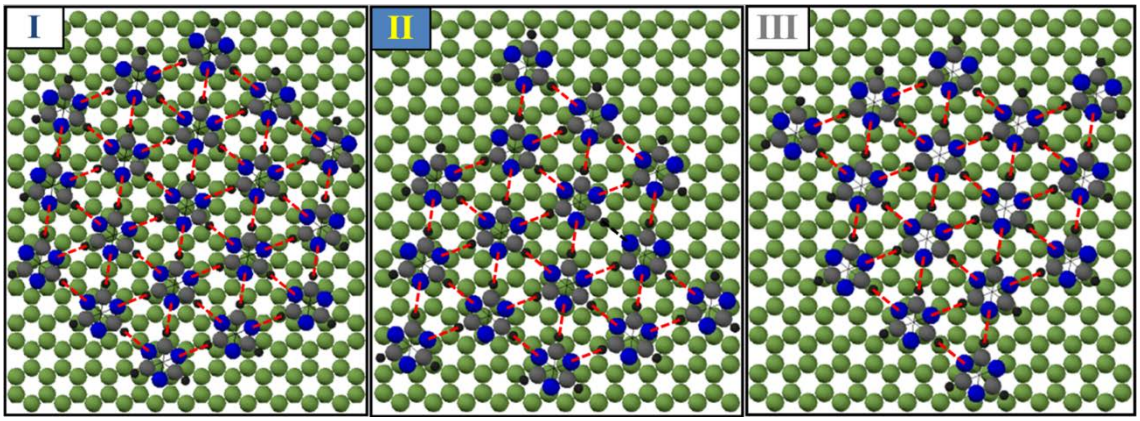

Figure S4. Zoom out of Zone I, II and III of the proposed model for the adsorption of triazine on graphene/Pt(111). The red dashed lines indicate the formation of C-H ⋯ N hydrogen bonds between adjacent molecules.