SUPPORTING INFORMATION:

Atomic-scale studies of molecular functionalization of graphene

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SUPPORTING TEXT

EXPERIMENTAL SECTION

Chemical synthesis of DHH-PTCDI. The N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) DHH-PTCDI was synthesized by reaction of perylene-3,4:9,10-tetracarboxylic di-anhydride (PTCDA, Aldrich) with 1-hexylheptylamine in imidazole (5h at 180°C).[1] 1-hexylheptylamine was obtained by reaction of 7-tridecanone and $NaBH_3CN$ in methanol (48h, RT), in the presence of excess ammonium acetate. Double-pass chromatography (chloroform/SiO_2) was used for final purification. The purity of the crystallized DHH-PTCDI molecules is estimated to be at least 99%.

STM & STS experiments. The STM experiments were performed in ultrahigh vacuum at room temperature (base pressure $3x10^{-11}$ Torr) using electrochemically etched tungsten tips followed by *in situ* electron bombardment. The I(V) curves were obtained by taking a number of individual I(V) curves either on the molecule or on the clean surface. The individual curves were then averaged followed by differentiation. Individual curves were obtained by a standard voltage ramp after opening the feedback loop (set-point +3V and 0.3 nA on the molecular layer, and various conditions on the graphene – see fig. 3). Each curve contains 200 points with delay and acquisition times of 640 μs for each point.

Surface preparation. A highly Nitrogen-doped (Resistivity: 0.04 Ω.cm; dopant density $3x10^{18}$ atoms·cm^{-3}) n-type 6H-SiC(0001) single crystal wafer was used. After formation of clean well reconstructed SiC(0001)-3x3 surface,[40,2] graphene was grown on SiC by 25 minutes annealing of the Si-terminated surface at 1325°C.[3] This gave an almost complete coverage of a single monolayer of graphene. The clean graphene surface was always checked in STM prior to molecule deposition (see Figure S1). The SAM was made by a 5-minute deposition of DHH-PTCDI at a crucible temperature of 200°C and a pressure of $1.2x10^{-10}$ torr (base pressure = $5.0x10^{-11}$ torr) on the RT graphene monolayer. Post annealing the sample

stabilized the molecular layer (~100°C for 10 minutes).[4]

ADDITIONAL STM RESULTS

The self-assembled monolayer (SAM) of DHH-PTCDI molecules on single layer graphene shows six different orientations (Fig. 1d). In order to determine the absolute orientation with respect to the underlying graphene, we need to know the orientation of the graphene. A typical STM image of the clean graphene prior to the formation of the SAM is shown in Fig. S1. The orientations of the graphene basal planes are marked. On all the samples we used, these are the same.[3] As a result, we find the SAM has two characteristic angles of -16°±1° and +8°±1° with respect to the underlying graphene. These correspond to the armchair and zig-zag conformations, respectively.

DETAILED DFT CALCULATIONS

To understand the adsorption of the DHH-PTCDI molecule on graphene in more depth, we provide here a detailed description of the DFT calculations. Our detailed calculations involve a complete optimization of the DHH-PTCDI molecule as a whole on the graphene substrate. Density Functional Theory (DFT) calculations were performed with the Vienna Ab-initio Simulation Package (VASP) code.[5] We compare the results from the different approximations using the DFT-D method. This allows us to apply both the general gradient approximation (GGA), the local density approximation (LDA),[6] and to include the Van der Waals (VdW) terms by using GGA-D. Standard projector augmented waves (PAW) pseudopotentials[7] are used. A Ceperley and Adler functional[8] parameterized by Perdew and Zunger[9] was applied to the LDA, while a Perdew-Burke-Ernzerhof (PBE-D)[10,11] functional with the GGA allows Van der Waals (VdW) forces to be modeled.[12] The LDA approximation has been used recently to calculate the adsorption of CoTPP molecule on a Cu(111) substrate[6] where the molecule-substrate interaction is driven by Van der Waals interactions. The LDA

method compensates for the lack of Van der Waals interactions by tending to overestimate binding energies. This weakness does not render such LDA calculations invalid.

To calculate the equilibrium distance between two DHH-PTCDI molecules as illustrated in Fig. S2, we have performed calculations using the GGA + van der Waals approximation and applied two procedures to calculate the equilibrium distance between two DHH-PTCDI molecules: (i) each molecule is relaxed separately in the gas phase to fix their position, before optimizing the molecule-molecule distance, (ii) each molecule is relaxed on the graphene, before optimizing the molecule-molecule distance. In the two procedures, we did not consider the graphene substrate during the optimization of the molecule-molecule distance, only the interaction energy between the two molecules as a function of the molecule-molecule separation was calculated. We used a cell 25 Å x 70 Å x 15 Å with 236 atoms in total. The smallest repeat distance between the molecules in two neighboring calculation cells is 15 Å. We have tried different size unit cells and they give the same result. Indeed, the energetic difference is less than 0.03 eV for a cell size increase of 5 Å in the x, y and z directions.

With these two simplified models of two DHH-PTCDI molecules, we found a minimum in the interaction energy variation versus the molecule-molecule distance 2.71 and 2.73 nm, respectively. This is 20 % larger than the observed experimental distance of 2.26 nm. While the molecule-molecule interactions between the alkyl chains appear to dominate the formation of brick wall structure of the self-assembled layer, other factors may influence the final structure. There are several possible explanations. Previous studies have already shown that the alkyl chains are very labile at room temperature even in an ordered molecular network[13], so they are not "fixed" as in the calculations. In addition, it is well known that such alkyl chains can fold; STM manipulation experiments have shown this.[14] It is quite probable that the chains fold into a "fork" shape rather than a "Y" shape (either in a static position, which we have not calculated or dynamically, which is beyond the scope of our calculations).

4

This folding could enable neighboring molecules to be closer. Furthermore, we do not know how the packing would be affected if a larger array of molecules were to be put into the calculation (for example, a 3 x 2 or 3 x 3 array). This is just too large a calculation to do.

Our calculations using LDA focused on the orientation of the molecule with respect to the underlying graphene layer. The number of atoms involved for the molecule and the surface is large, so we chose a simple PTCDI molecule without any alkyl chains, physisorbed on a graphene slab (Fig. S3). This enabled the calculation in LDA to be kept to a manageable size. The resulting relaxed molecular configurations (zig-zag and arm-chair) are shown in Fig. S4, and the calculated adsorption energies in the first two lines of Table I.

To have a complete picture, we performed thorough calculations with a single DHH-PTCDI molecule complete with alkyl chains on a single free-standing graphene layer. We have used the DFT-D method in VASP 5.2 which enables the Van der Waals (VdW) forces to be modeled within the GGA. These are implemented using the Perdew, Burke, and Ernzerhof functionals (PBE-D).[10,11] This is important if we wish to take into account the alkyl chains properly. The results of the calculations are shown in Figs. S5 to S8.

In a first step, we calculated the PTCDI adsorption on graphene taking into account different approximations such as increasing the cutoff energy or relaxing the graphene layer. The results are presented in table I.

Table I	Adsorption energy: armchair	Adsorption energy: Zig-zag	ΔE (zig-zag minus armchair)
-LDA -Cutoff=400 eV; F<0.04 eV/Å -Graphene layer is fixed	-0.84 eV	-0.94 eV	-0.1 eV
-LDA -Cutoff=400 eV; F<0.01 eV/Å -Graphene layer is fixed	-0.84 eV	-0.95 eV	-0.11 eV

-GGA -Cutoff=400 eV; F<0.01 eV/Å -Graphene layer is fixed -Without dispersive terms	+0.48 eV	+0.53 eV	+0.05 eV
-GGA -Cutoff=400 eV; F<0.01 eV/Å -Graphene layer is fixed -With dispersive terms	-1.52 eV	-1.63 eV	-0.11 eV
-GGA -Cutoff=400 eV; F<0.01 eV/Å -Graphene layer is allowed to relax -With dispersive terms	-1.56 eV	-1.67 eV	-0.11 eV
-GGA -Cutoff=500 eV; F<0.01 eV/Å -Graphene layer is fixed -With dispersive terms	-1.51 eV	-1.61 eV	-0.1 eV

There are a number of conclusions that can be derived from the comparison between the LDA and GGA calculations. First, if the dispersive terms are not included, the LDA method indicates that adsorption occurs while the GGA does not. When the dispersive terms are added, adsorption is always favorable regardless of the method used. Each calculation method is applied to both the armchair and zig-zag configurations. In all cases, the zig-zag model is energetically favored with respect to armchair one, and the energy difference is both constant and small. Increasing the cutoff energy, the convergence energy limit, or allowing the graphene layer to relax does not modify either the calculated adsorption energy or the preference for the zig-zag configuration.

In a second step, we have calculated the energy adsorption of the DHH-PTCDI molecule on graphene. Based on the analysis of the STM images, we considered two configurations of the DHH-PTCDI molecule oriented with respect to the underlying graphene lattice: armchair and zig-zag. The gas-phase configurations of the DHH-PTCDI molecule are shown in Fig. S5. Two configurations were found where the perylene core is positioned

6

differently with respect to the alkyl chains; tilted and twisted. These two configurations are presented in parts (a) and (b) of Figs. S6, S7 and S8 for three different relaxed configurations. There are now 454 atoms in a cell of 34.51 Å x 29.58 Å x 15 Å. Due to the larger cell we took into account one Γ-point only. Despite the large number of atoms, in the DHH-PTCDI-graphene system, these different tests could be carried out, though the amount of CPU time required was enormous compared to GGA or LDA calculations. The molecule is allowed to relax while the graphene layer is maintained in a fixed position. The atoms were relaxed until atomic forces were smaller than 0.01 eV per Å and the energy cut-off is equal to 415 eV. Our calculations indicate that the energy difference between the armchair and zig-zag adsorption configurations of DHH-PTCDI on graphene is reduced with respect to the PTCDI-graphene system.

Table II	Adsorption energy: armchair	Adsorption energy: Zig-zag	ΔE (zig-zag minus armchair)
-GGA -Cutoff=400 eV; F<0.01 eV/Å -Graphene layer is fixed -Without dispersive terms	-0.01 eV	-0.04 eV	-0.03 eV
-GGA -Cutoff=400 eV; F<0.01 eV/Å -Graphene layer is fixed -With dispersive terms	-2.17 eV	-2.22 eV	-0.05 eV
-GGA -Cutoff=415 eV; F<0.01 eV/Å -Graphene layer is fixed -With dispersive terms	-2.18 eV	-2.22 eV	-0.04 eV

To complete the information concerning the finer details of the calculations: we used a smearing equal to 0.05 eV; for the valence electrons, the projector augmented waves (PAW) pseudopotential for the GGA-PBE (Perdew-Burke-Ernzerhof) functional was used. In the VASP code, electronic optimization was considered to be achieved if the total energy change and the eigenvalues change between two steps are both smaller than 10^{-4} eV. At that

point, the relaxation of the electronic degrees of freedom was stopped. Finally, for comparison with the STM images, the local densities of states calculations were performed using the Tersoff-Hamann approximation.[15]

SUPPORTING FIGURES

Fig. S1
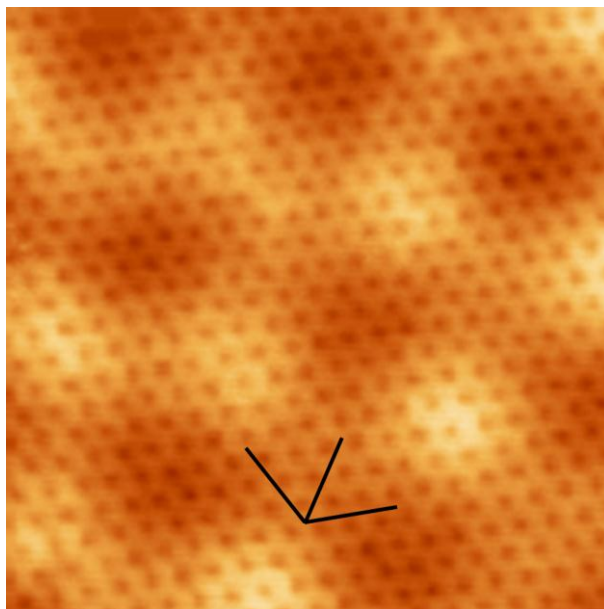
A 6 x 6 nm STM topography of the clean monolayer graphene after epitaxial growth on SiC (-100 mV, 0.5 nA). The brighter regions with a 2 nm periodicity correspond to the underlying buffer layer. The three black lines indicate the basal-plane directions of the graphene monolayer which are always the same on the samples we used. This allows us to determine the absolute orientation of the DHH-PTCDI layer even though we can no longer see the graphene.

Fig. S2
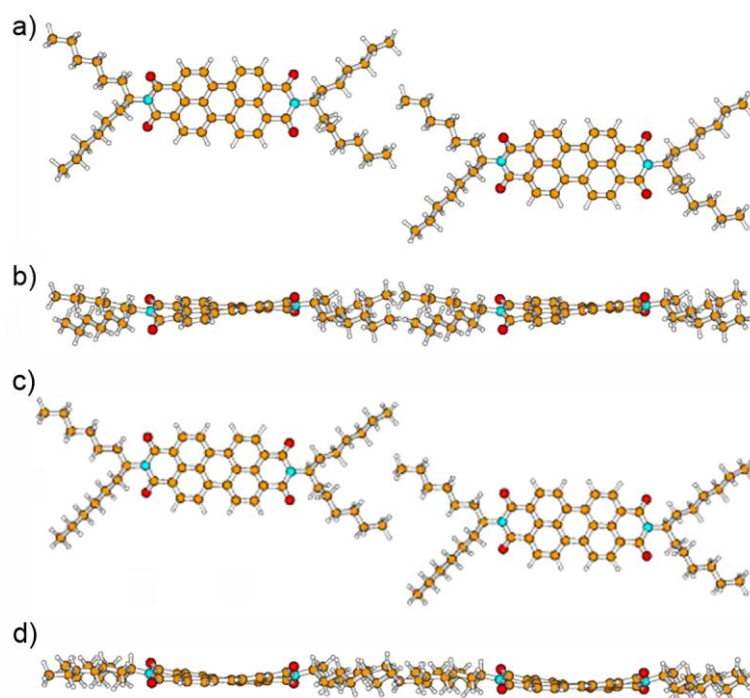
The ball and stick model of two DHH-PTCDI molecules showing the packing of the alkyl chains. (a) Top view, and (b) side view of the positions of the molecules optimized in the gas phase (corresponding to (c) and (d) in Fig. S5). (c) top view and (d) side view with optimization on the graphene (corresponding to Fig. S7) The molecule-molecule separation was subsequently calculated. The cell used is 25 Å x 70 Å x 15 Å with 236 atoms in total. The equilibrium molecule-molecule distances of the lowest energy configuration in the framework of the GGA+VdW approximation, for (a) and (c), are 2.71 and 2.73 nm, respectively.
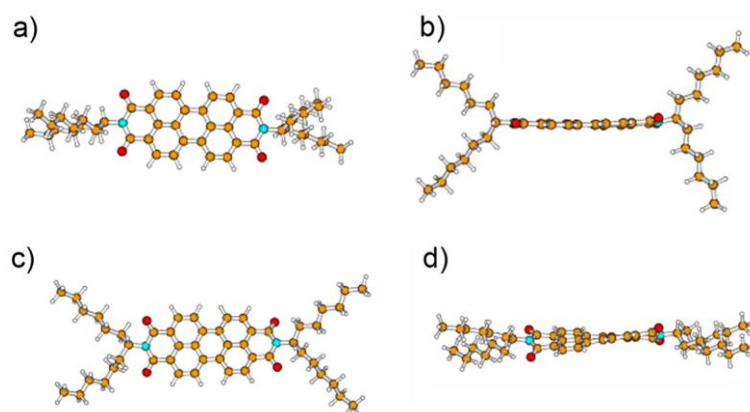
Fig. S3

a)

b)
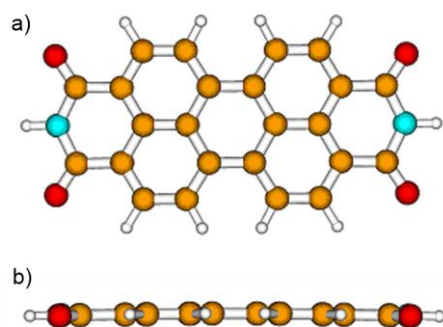
Gas phase structure of the PTCDI molecule (with no alkyl chains) used initially to calculate the adsorption energy on a single graphene layer. (a) top view, (b) side view. See Fig. S4 for the molecule and the graphene layer.
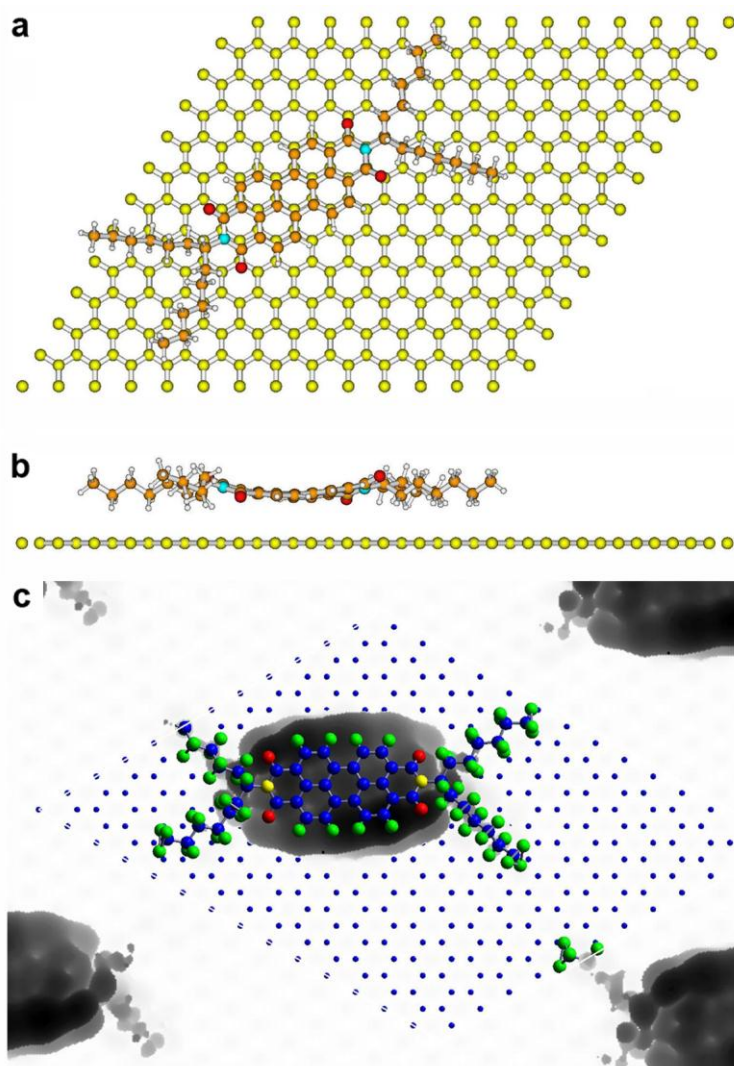
Fig. S4
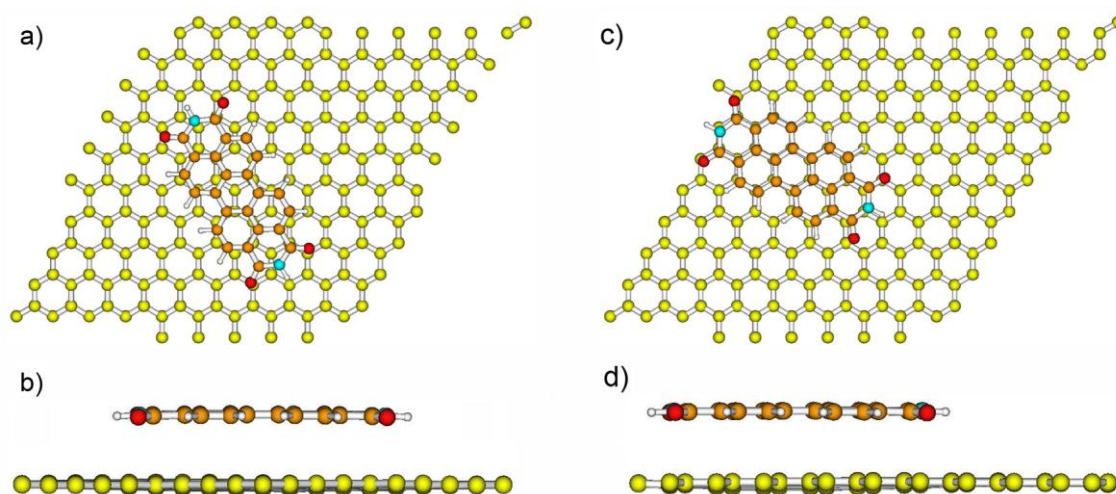
Relaxed structure of the PTCDI molecule (with no alkyl chains) on a single graphene layer. (a) top view, and (b) side view of the molecule orientated in the zig-zag configuration with respect to the graphene layer. The graphene slab is 24.65 Å along each side of the rhombus. In the GGA+VdW, the adsorption energy = -1.67 eV. (c) top view, and (d) side view of the molecule orientated in the armchair configuration. The calculated adsorption energy is -1.56 eV. The carbon atoms of the molecule are in orange while those of the graphene layer are in olive so that the molecule can be easily distinguished.
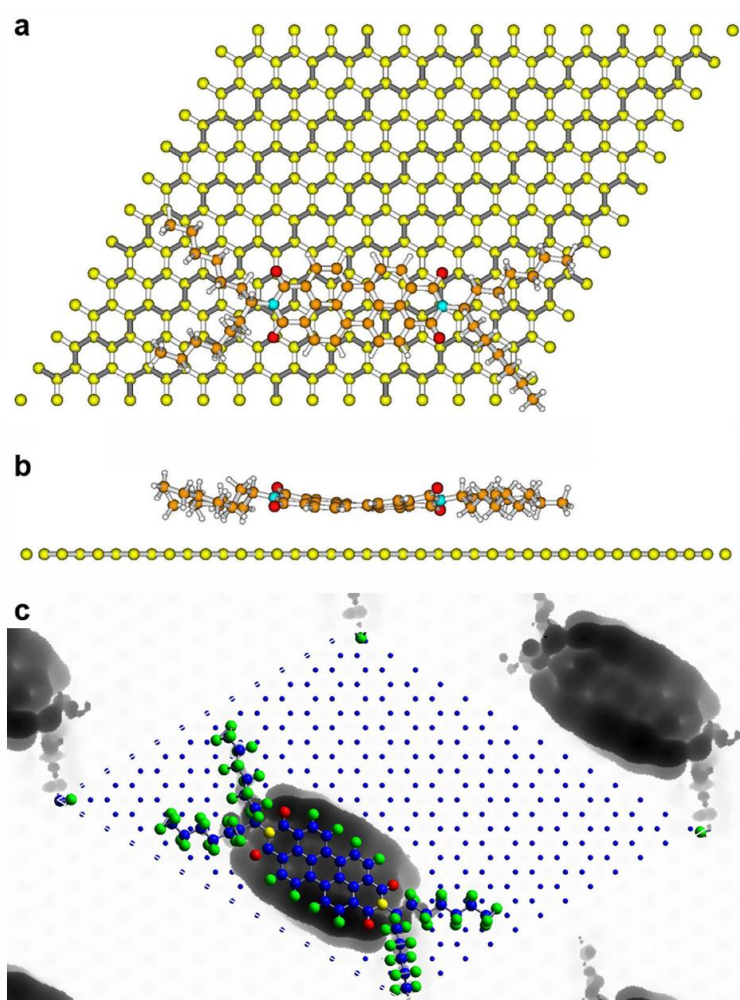
Fig. S5

Gas phase structures of the DHH-PTCDI molecule, including the alkyl chains, used to calculate the adsorption energy on a single graphene layer within the GGA+VdW framework. Two molecular configurations were found; (a, b) tilted, and (c, d) twisted. (a, c) top views, (b, d) side views, respectively. See Figs. S6-S8, for the relaxed molecular configurations on the graphene layer. The tilted model is the most stable (the energy difference between the two models is $\Delta E=0.20$ eV).
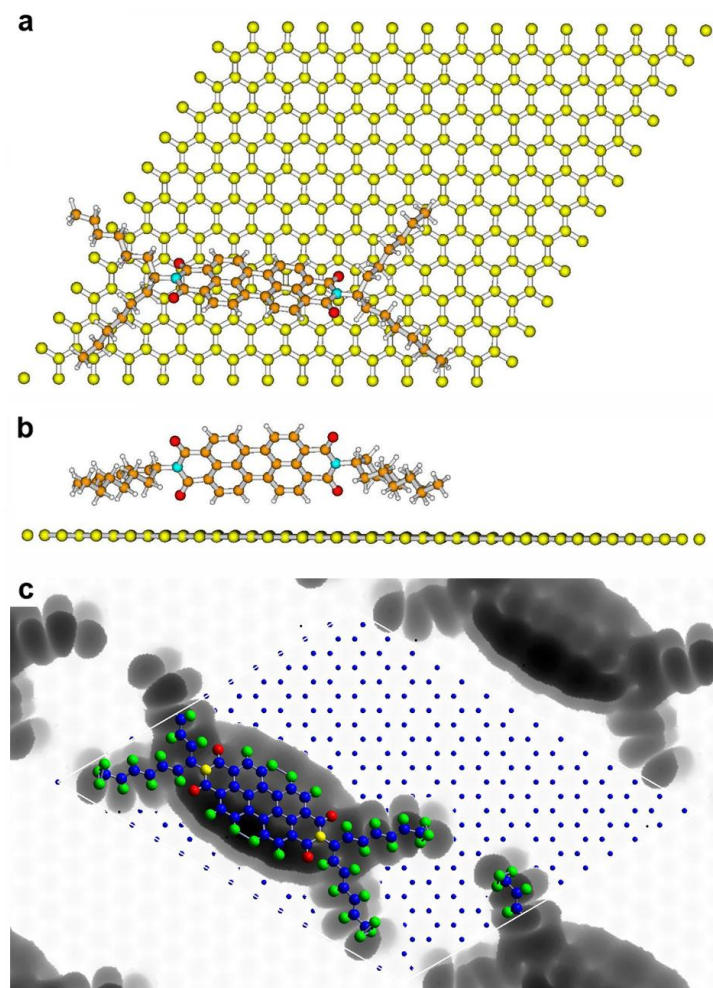
Fig. S6

Relaxed structure of the DHH-PTCDI molecule on a single graphene layer. The molecule is *twisted* and orientated in the *arm-chair* configuration with respect to the underlying graphene. The DHH-PTCDI molecule including the alkyl chains requires a larger graphene slab: 34.51 Å x 29.58 Å. (a) top view, and (b) side view. In (a) and (b), the carbon atoms of the molecule are in orange to distinguish them form the carbon atoms of the graphene layer (olive). (c) Shows the calculated local density of states (LDOS) plotted as an isodensity map integrated over the energy window between E_F and E_F+3 eV (isodensity=1.5 e$^-$/Å^3).

Fig. S7

Relaxed structure of the DHH-PTCDI molecule on a single graphene layer. The molecule is *twisted* and orientated in the *zig-zag* configuration with respect to the underlying graphene. The DHH-PTCDI molecule including the alkyl chains requires a larger graphene slab: 34.51 Å x 29.58 Å. (a) top view, and (b) side view. In (a) and (b), the carbon atoms of the molecule are in orange to distinguish them form the carbon atoms of the graphene layer (olive). (c) Shows the calculated local density of states (LDOS) plotted as an isodensity map integrated over the energy window between E_F and E_F+3 eV (isodensity=1.5 e$^-$/Å^3).

Fig. S8

Relaxed structure of the DHH-PTCDI molecule on a single graphene layer. The molecule is *tilted* and orientated in the *zig-zag* configuration with respect to the underlying graphene. The DHH-PTCDI molecule including the alkyl chains requires a larger graphene slab: 34.51 Å x 29.58 Å. (a) top view, and (b) side view. In (a) and (b), the carbon atoms of the molecule are in orange to distinguish them form the carbon atoms of the graphene layer (olive). (c) Shows the calculated local density of states (LDOS) plotted as an isodensity map integrated over the energy window between E_F and E_F+3 eV (isodensity=1.5 $e^-/Å^3$). The adsorption energy is equal to -1.98 eV.

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