DFT-D Study of Adsorption of Diaminoethane and Propylamine Molecules on Anatase (101) TiO_2 Surface

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Abstract

The adsorption on anatase (101) TiO_2 surface of two model amines, diaminoethane (DAE) and propylamine (PPA), was investigated using Density Functional Theory-Dispersion included (DFT-D) calculations. The investigated coverage is ranging from 0.25 monolayer to full coverage (one amine molecule per surface Ti ion). Both interactions of the adsorbed layer with the anatase (101) TiO_2 surface and intermolecular interactions are described. A structural transition from a bridge to a perpendicular structure is found for DAE when evolving from 0.25 monolayer to full coverage. At full coverage, a dense, ordered adhesive layer is formed. For DAE, at intermediate coverage, different isoenergetic configurations are found and structural transition from a bridge to a perpendicular structure is found. In contrast, the adsorption mode of PPA is more regular with only perpendicularly adsorbed molecules at all investigated coverages. Dispersion forces already account for 40% of the adsorption energy at low coverage (0.25 ML) and are the driving force for monolayer formation with a

contribution of 60% up to 100% at high coverage. As revealed by molecular dynamics, the molecules can change their orientation towards the surface in a concerted way.

Keywords

Adhesion, amine, cohesive film, DFT-D, diaminoethane, propylamine, TiO_2

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Introduction

Model amines are often used to investigate the epoxyamine-Ti interactions at the molecular level (see Ref [1] and references therein). A reliable adsorption of amines moieties on the surface is a key point for adhesion. The study of such organic/inorganic interfaces is thus challenging and modeling approaches can help to disentangle the hard-soft matter interactions at the atomic scale.

Adsorption of several bio- and organic molecules on TiO_2, including amines, has been reviewed.[2,3] Farfan-Arribas and Madix[4] used amine adsorption to determine the Lewis acidity of surface Ti^{4+} ions in rutile TiO_2 (110) surfaces. Ethylamine and diethylamine were both found to adsorb on the stoichiometric surface through formation of N–Ti bonds. On defective surfaces bonding also occurred at oxygen-vacancy sites. In both cases the amines remained intact but on the defective surface less amines were adsorbed. The authors suggested that this might be due to adsorption at the defect sites blocking adsorption at more than one neighbouring Ti^{4+}site. The desorption activation energy decreased in the order diethylamine > ethylamine > ammonia which is also the order of decreasing Lewis basicity. The authors suggested that this was an evidence of adsorption driven by a Lewis acid–base interaction with the Ti^{4+} ions behaving as Lewis acid sites (LAS). Other DFT works on adsorption of arginine showed an adsorption of the lateral NH_2 moiety on TiO_2 with a rather strong energy of adsorption (1.4 eV on rutile (110)[5], 2.8 eV on (100) anatase[6] and 1.5 eV on (001) anatase[7]). Recently we showed that diaminoethane (DAE), a model amine molecule, can adsorb on TiO_2 by substituting water molecules and form a full monolayer.[1] Our DFT study of the adsorption of a full layer of diaminoethane on anatase (101) TiO_2 concluded to an interaction energy of around 0.5 eV (0.7 eV with dispersion forces included).[1] A thermodynamic approach was therefore used to bridge the gap between calculations at 0K under vacuum and solid/liquid interface.[1]It was found that the water substitution by DAE to form a full DAE layer is favorable for a large range of DAE concentration in toluene.[1] The purpose of the present work is to complement the previous approach with more insight into the mechanisms of the monolayer formation. Indeed, our previous work was conducted in considering only one adsorption mode, with DAE forming one single bond with the surface. However, DAE possesses two NH_2 functional groups, which can play a role in the adhesion with the surface. This can be a problem for some applications because of i) a mixture of different adsorption modes that may lead to a disordered layer, ii) the hindering of the reactive moiety for further adhesion to a subsequent adsorption, e.g. for polymer layers.

In the present paper, using first-principles calculations, our first aim is to further explore different adsorption modes of diaminoethane (DAE) molecules on anatase (101) TiO_2 surface. Moreover we also investigate the adsorption of another model amine molecule, the propylamine (PPA), on the anatase (101) TiO_2 surface. PPA exhibits one single active moiety, supposed to react with surface Ti^{4+} atoms, whereas DAE is a bifunctional molecule with two amine group terminations, which may bind – or not – through both amines to the Ti^{4+} surface cations. These two molecules could thus have a different topological behavior when interacting with the substrate. The assembling of the molecules at the surface of the TiO_2 substrate is studied by varying the coverage from 0.25 monolayer (ML) (one amine molecule every four surface Ti atoms) to 1 ML (one amine molecule per Ti atom). The interaction of the formed layer with the surface is evaluated through Density Functional Theory-Dispersion included (DFT-D) calculations to provide clues on the adhesive properties of the films.

In this paper, we also focus and discuss dispersion contributions, by performing systematic DFT and DFT-D calculations for all adsorption modes. Dispersion interactions appear to be crucial when one considers self-assembled organization of molecules onto a surface that could change drastically adsorption mode in the study of the molecular assembly with surface interaction.[8]

Method

Details of calculations

The periodic calculations were performed using the DFT method based on the GGA approximation employing the rPBE[9,10] exchange-correlation functional as implemented in the plane-waves program VASP.[11,12] The projector-augmented wave (PAW) potentials[13,14] were used for the core electron representation with a PAW core radius of 1.52 Å for oxygen. With plane waves methods, the quality of the basis set is determined by a single parameter, the cut-off energy E_{cut}. We used a converged value of E_{cut} = 400 eV. The integration in reciprocal space was performed with a Monkhorst-Pack grid.[15]

The bulk cell parameters for anatase TiO_2 were calculated as a_{calc}= 3.864 Å, c_{calc}= 9.707 Å, values in agreement with experimental (a_{exp}= 3.776 Å and c_{exp}= 9.486 Å)[16] and other data determined with the same method.[17] The anatase (101) TiO_2 surface was modeled by a periodic slab depicted in Figure 1. The unit cell was (1 x 2) in the [010] and [10-1] directions respectively. The cell was composed by a total number of 72 atoms with 24 titanium atoms and 48 oxygen atoms corresponding to a cell dimension of 10.3 x 7.6 x 43 $Å^3$ with a surface area of 78.28 $Å^2$. The cell exposed four Ti^{4+} cations. We studied four coverages, adding one to

four molecules in the cell, thus from one molecule each four Ti^{4+} to one molecule per Ti^{4+} cation. A vacuum zone of 33 Å in the z direction was used to create a surface effect. 12 Ti and O atoms were frozen in their bulk positions at the bottom of the cell to simulate a bulk effect. All other atoms were free to relax. The periodic slab was repeated in the three directions. A k-point mesh of (2x2x1) was used.

The anatase (101) TiO_2 surface exhibits two types of atoms (Figure 1a and 1b): the topmost atoms are five-fold coordinated Ti atoms (four atoms Ti5c – referred as Ti^{4+} in the following) and two-fold coordinated O atoms (four atoms O2c). The other atoms considered in the bulk position are six-fold coordinated Ti atoms (Ti6c) and three-fold coordinated O atoms (O3c).

A dipolar correction was introduced along the z axis perpendicular to the surface to take into account the spurious polarity induced by the non equivalence of the top and bottom surfaces. This procedure was carefully validated in recent works.[1,18]

The isolated diaminoethane (DAE) and propylamine (PPA) molecules (see Figure 2) were relaxed in the same simulation cell as the anatase (101) TiO_2 slab. Because of the existing free rotation around the C_2-C_3 bond for both molecules, two representative geometries were chosen to study different configurations of the adsorbed molecules on the surface (average orientation of the molecule to the surface) and different conformations for each configuration (local orientation of the NH_2 ends versus the C_2-C_3 backbone): one conformation (referred as E) with the two terminal groups (NH_2/NH_2 or NH_2/CH_3) away from each others (linear arrangement of the C-C backbone, Figure 2) and the other conformation (referred as Z) with the two terminal groups in closer proximity (bent arrangement of the C-C backbone, Figure 2). We here use the notation E-Z, as reminiscent of nomenclature used to distinguish structural cis/trans stereoisomers. Since both molecules give equivalent relaxed energies for E and Z conformations, as a consequence of the free rotation around the C_2-C_3 bond, both conformations of each amine molecules have been considered for adsorption study in the following.

Amines were adsorbed by approaching the molecules above the LAS, Ti^{4+} atoms of the anatase (101) TiO_2 surface, which have been demonstrated to be the adsorption sites of diaminoethane.[1] In the starting configurations, a Ti-N bond was formed, respecting the directionality of the Ti-O bonds in the bulk anatase TiO_2 structure. As four surface five-fold coordinated Ti^{4+} atoms are available in the (1x2) simulation cell, it enables the study of the

adsorption of one to four molecules, corresponding to increasing coverage (θ= 0.25, 0.50, 0.75 and 1 ML) of DAE and PPA molecules, thus exploring the pathway from a single amine molecule adsorption towards monolayer formation above the anatase (101) TiO_2 surface.

To explore the influence of van der Waals (vdW) forces on the adsorption topologies and energetics, we performed systematically successive calculations in the DFT and DFT-D schemes using D2 Grimme's formalism as implemented in VASP.[19,20] Geometries were generally only slightly affected by vdW forces: a slight shortening of Ti-N bond length (-2%) was observed when the vdW forces were included. If not stated otherwise, the energetic quantities given in the text are the one calculated with the DFT-D method.

Energetic considerations

In this paper, the adsorption energies ΔE_{ads} are calculated using the following formula:

$$\Delta E_{ads} = \left(E_{total}(mol + surf) - n \times E_{opt\ isol}(mol) - E_{opt\ isol}(surf)\right)$$

where $E_{total}(mol + surf)$ is the total energy of the system with n amine molecules adsorbed on the anatase (101) TiO_2 surface, $E_{opt\ isol}(mol)$ and $E_{opt\ isol}(surf)$ are the total energies of the relaxed isolated molecule and surface, respectively, and n is the number of adsorbed molecules on the surface. Absolute values of adsorption energies are reported in the paper. In this way, positive values indicate exothermic adsorption. In the following, adsorption energies are given as total adsorption energy per cell, in order to compare the surface energy gain at different coverages. When adsorption energy per molecule is calculated, it will be mentioned specifically in the text. ΔE_{ads} can be decomposed into several contributions:

$\Delta E_{ads} = \Delta E_{ads\ KS} + \Delta E_{ads\ disp}$ where $\Delta E_{ads\ KS}$ is the Kohn-Sham contribution to the adsorption energy and $\Delta E_{ads\ disp}$ is the dispersion energy. This dispersive energy can be decomposed into the molecules/surface interaction and the intermolecular interactions in the organic layer, $\Delta E_{ads\ disp} = \Delta E_{disp}(mol\ /\ surf) + \Delta E_{disp}(mol/mol)$. This allows us in particular to analyze the contribution of the dispersion forces $\Delta E_{disp}(mol/mol)$ in self-assembling in the case of a full monolayer. It is given by

$\Delta E_{disp}\left(\frac{mol}{mol}\right) = \Delta E_{disp}\,(layer) - \Delta E_{disp}\,(isolated\ molecule)$ and $\Delta E_{disp}\,(layer)$ is obtained by a single point calculation of the dispersive energy in vacuum of the monolayer in the adsorbed geometry and $\Delta E_{disp}\,(isolated\ molecule)$ is the dispersive energy of the isolated molecule in the same geometry as in the monolayer.

Note that all energies are evaluated at 0K. In our previous study[1] we proposed a whole thermodynamic approach to predict the conditions of the diaminoethane layer formation on anatase as a function of the partial pressure of water in the system. The purpose of the present work is to complement the approach with more insight into the mechanisms of the monolayer formation on a dry anatase surface.

We performed a detailed analysis of zero point energy (ZPE) contributions to adsorption energies in our previous work.[1] This was necessary to provide the most precise evaluation of free energies of adsorption of DAE on anatase. In the present work, the ZPE contributions to adsorption energies were found to be 0.10 and 0.17eV at the lowest and highest coverage, respectively. These small contributions as compared to the calculated energies of adsorption are not included in the energies of adsorption.

Activation barriers have been determined along the Minimum Energy Path using a drag method. Here, the system is minimized while one coordinate is held fixed while all other coordinates of freedom in the system are relaxed. The maximum energy corresponds to the transition state and determines the activation barrier. In the following investigated paths, the drag coordinate is chosen toward z-axis perpendicular to the surface.

Born Oppenheimer Molecular Dynamics

DFT-based Born-Oppenheimer molecular dynamics simulations were performed with the CP2K/Quickstep package, using a hybrid Gaussian and plane wave method for the electronic representation.[21] The Perdew-Burke-Ernzerhof (PBE)[22] exchange-correlation density functional was used. Goedecker-Teter-Hutter pseudopotentials (GTH),[23] a triple zeta plus polarization Gaussian basis set (TZVP) for the orbitals and a density cutoff of 400 Ry were used. Only for titanium atom a double zeta plus polarization Gaussian basis set (DZVP) was employed. Dispersion forces were taken into account with the Grimme DFT-D2 method.[19,20] The anatase (101) TiO_2 surface was constructed using a slab model having a (1×4) surface unit cell (10.32 Å x 15.15Å) with a 26 Å vacuum region between the slabs. Periodic boundary conditions were applied in all directions of space. It was large enough in the three directions to ensure convergence of the wavefunction at the Gamma point. On one side of the slab the anatase (101) TiO_2 surface was saturated by a monolayer of DAE molecules. The overall stoichiometry of the slab is $48TiO_2$ +8DAE. Dynamics of 10 ps were conducted in the microcanonical NVE ensemble (after equilibration is achieved through canonical NVT dynamics) with a time-step of 0.5 fs. Average temperature was around 300± 11 K.

Results: Amine adsorption process: structures and energies

Adsorption of DAE on the anatase (101) TiO_2 surface

We consider the adsorption process of DAE molecules forming zero (physisorption, *Ph*), one (perpendicular chemisorption, *P*) or two (bridge chemisorption, *Br*) N-Ti bonds. When several molecules are adsorbed, we just mention their adsorption mode, for instance *BrBr*, *BrP*, *PP* for two adsorbed molecules, *BrBrP*, *BrPP* for three adsorbed molecules, etc. The subscript E or Z is added to indicate the conformation of the adsorbed species on the TiO_2 surface. Finally, when two molecules are adsorbed in the *P* mode, they may be aligned along the [010] or the [11-1] directions as described on Figure 1, and this will be also notified.

θ=0.25 ML. Studying this coverage (1.28 molecule/nm^2) enables us to perform a comprehensive and detailed study of the interaction between a single amine molecule (one molecule per cell) and the anatase (101) TiO_2surface without molecule-molecule lateral interaction (we checked that the size of our simulation cell is large enough to ensure no interaction between periodic images). We determined several chemisorbed states with a combined formation of Ti-N bonds and H bonds from both the NH_2 ends to surface oxygen O2catoms. All these adsorbed configurations are shown in Figure 3 where the adsorption energies and bond lengths are also given. In the *P* adsorption mode, the two configurations P_E and P_Z are isoenergetic (ΔE_{ads}=1.06 eV). The Ti-N average bond length is 2.32±0.03 Å and the Ti-N bond always follows the directionality of the bulk Ti-O bonds. Depending on the E or Z conformer and the orientation with respect to the surface, the DAE molecule exhibits weak H bonds with the surface through the adsorbed-amine hydrogen atoms pointing towards surface O2c atoms. The H-O distances are 2.43 Å and 2.48 Å for the E conformation (Figure 3b), and they are 2.35 Å and 2.78 Å when the adsorbed DAE is in the Z form (Figure 3c) with one hydrogen atom of the adsorbed amine group interacting with one O2c atom (H-O distance: 2.35 Å) and the hydrogen atom of the non adsorbed second amine group pointing towards a surface oxygen atom O2c (H-O distance: 2.78 Å). Other isoenergetic configurations studied by tilting the molecule towards the [010] or [11-1] directions (see Table SI in the supplementary materials) suggest that the adsorbed DAE molecule is free to rotate around the Ti-N bond, highlighting the capability to bend in different directions towards the surface at low coverage, switching from E to Z conformation as schematized in Figure 3a.

In contrast, in the *Br* adsorption mode, one unique configuration is stable (Figure 3d) and it is parallel to the [010] direction, in a 'bridge' conformation between two Ti atoms. The Ti-N bond lengths are 2.32 Å and 2.37 Å and two weak additional NH-O2c hydrogen bonds (2.47 Å and 2.50 Å) are present. The adsorption energy is ΔE_{ads}=1.45 eV in this *Br* mode, more favorable by 0.39 eV compared to the *P* modes. This difference is maintained when considering the differences in the rotational entropy contributions of the *P* and *Br* modes, which is of the order of RT. In the *Br* configuration, the molecule is deformed in geometry in between E and Z forms (measured N-C-C-N dihedral angle of 102°). Such a bridge conformation is not possible along the [11-1] direction because of steric hindrance due to the O2c surface atoms. If we calculate average interaction energy for one NH_2 group, we find a value of 1.05 eV for the *P* configuration and a value of 0.725 eV/NH_2 group for the *Br* configuration. In other words, when the DAE molecule is bonded to two Ti cations, the bond with each Ti is weaker than when it is adsorbed on one single Ti.

We also investigated the pathway from the *P* to *Br* topology using a drag method. The associated energetic barrier is of E_{act} (DFT) = 0.08 eV and it does not exist when dispersion is considered due to the metastability of *P* adsorption mode at low coverage coming from the high flexibility of Ti-N bond in *P* mode as described before. The back reaction from *Br* to *P* topology requires higher activation energy of 0.39 eV. This value is under-estimated when dispersion forces are not included (standard DFT calculated value: 0.21 eV). We can notice here that van der Waals contributions impact drastically calculation of activation barriers and therefore must be taken into account. Considering both thermodynamics and kinetics, the data indicate that at low coverage, the *Br* mode will be favored.

θ=0.50 ML. Similar analysis of the possible conformations of DAE on the surface was done for a coverage θ = 0.50 ML (2.57 DAE molecules/nm^2). Several adsorption modes for the two adsorbed molecules were investigated: *BrBr*, BrP_E, BrP_Z, P_EP_E, P_ZP_Z, P_ZP_E.

In the *BrBr* mode (Figure 4a), both DAE molecules form [010] bridges on the surface, as at lower coverage. At this coverage and in this *BrBr* adsorption mode, all Ti^{4+} atoms of the surface are involved in Ti-N bonds. The total adsorption energy per cell is ΔE_{ads}=2.50 eV, i.e. 1.25 eV per molecule. This adsorption process is thus exothermic, but slightly less exothermic that the adsorption of a single DAE (1.45 eV). This decrease of energy gain per molecule can be explained by structural modifications in the two DAE *Br* adsorption mode (compared to

the adsorption of one DAE isolated molecule) and Ti-N bond lengths increase from 2.32 Å to 2.35 Å and from 2.37 Å to 2.40 Å and 2.42 Å when two DAE molecules are adsorbed.
The *BrBr* adsorption mode (figure 4a) is isoenergetic to the BrP_Z configuration (ΔE_{ads}=2.58 eV, see Figure 4b), where the DAE molecule in P_Z configuration is stabilized by the formation of a H bond with a surface O2c atom. There is also a BrP_E configuration (not shown) for the two DAE molecules with an adsorption energy of 2.36 eV, less stable than the BrP_Z configuration. For the molecule evolving from the *Br* to P_Z transition, that is the more stable *BrP* configuration, the Ti-N bond attached to the surface changes from 2.35 Å to 2.33 Å and the Ti-N bonds of the *Br*-DAE adsorbed molecule are reduced from 2.40 Å to 2.38 Å. The associated activation energy for the Br to P transition estimated using drag method is 0.27 eV (0.10 eV without vdW contributions), so that the *Br* to *P* transition could occur to release steric effects. This latter BrP_Z configuration can be an intermediate configuration adopted by DAEs to liberate a Ti^{4+} site for the adsorption of another molecule, and thus increase the surface coverage.

In the *PP* mode (some configurations are schematized in figure 4c and 4d), due to the asymmetric environment of each Ti^{4+} surface site, the two DAE molecules can be aligned either along the [010] or [11-1] direction (mode A: *PP*[010] and mode B:*PP*[11-1] respectively). The P_EP_E[010] and P_EP_E[11-1] adsorption modes are nearly isoenergetic with an adsorption energy of average value 2.01 ± 0.04 eV, Figure 4c and d whereas the P_ZP_Z[11-1] configuration is more stable than the P_ZP_Z[010] one (2.08 eV *vs*. 1.50 eV). Indeed, as the vicinal Ti-Ti distances differ in the [010] and [11-1] directions (3.78 Å and 5.48 Å respectively), steric hindrance is responsible for the lower adsorption energy calculated for the Z conformation with respect to E conformation in the *PP*[010] topology. We observe that in the [010] direction, Ti-N bonds are longer compared to the [11-1] direction, even more when the molecule occupies more space like in Z conformation: Ti-N bonds have increased from 2.30 Å in the case of one adsorbed P_E to 2.32 Å and 2.33 Å in [11-1] and [010] directions, respectively and from 2.30 Å in the case of one adsorbed P_Z to 2.32 Å and 2.36 Å in [11-1] and [010] directions, respectively. Finally, we can conclude that the *PP* adsorption mode exhibits three isoenergetic configurations, P_EP_E[010], P_EP_E[11-1] and P_ZP_Z[11-1], which remain however less stable than the *BrBr* and BrP_Z ones.
We will demonstrate below that the increase of the Ti-N bond lengths when two DAE molecules are adsorbed, i.e. as observed in *BrBr*, shows a decrease of the Kohn Sham

contribution in the total adsorption energy. More details about the contributions of the different forces will be provided in the following (comments on Figure 9).

θ=0.75 ML. At this coverage, corresponding to three molecules per cell, the following configurations were considered, as schematized in Figure 5:

i) The physisorption (*Ph* mode) of an additional DAE molecule on the *BrBr*[010] configuration obtained at 0.5 ML. It results in the *BrBrPh* configuration, with an adsorption energy of ΔE_{ads}=2.73 eV,
ii) BrP_EPh configuration, with ΔE_{ads}=2.93 eV. Interestingly, the BrP_EPh mode is stabilized over the *BrBrPh* configuration and a Ti^{4+} atom is now available for the next step of adsorption,
iii) BrP_EP_E (ΔE_{ads} = 3.07 eV) or BrP_ZP_Z (E_{ads} = 2.84 eV) configurations, and
iv) finally the *PPP* mode (with ΔE_{ads} =2.96 eV and 2.46 eV in the P_E and P_Z modes, respectively)

We note that the most stable configurations, BrP_EP_E and $P_EP_EP_E$ are nearly isoenergetic, revealing some degrees of freedom of the molecule adsorbed in the half-filled [010] direction. Moreover we showed that the transition from the *Br* to the *P* mode starting from BrP_EP_E to reach $P_EP_EP_E$ adsorption mode is associated to a small activation energy of 0.27 eV (DFT-D). In the $P_EP_EP_E$ mode, all the Ti-N bonds are shortened compared to BrP_EP_E. We also notice that when the coverage increases, the E form is stabilized over the Z form for steric reasons.

θ=1.00 ML. Finally, a full monolayer is obtained by adding a fourth DAE molecule on the surface of the slab chosen as a model of the TiO_2 surface (Figure 6). Obviously, the only configuration is the *PPPP* one. The $P_EP_EP_EP_E$ configuration (3.86 eV) is more stable than the $P_ZP_ZP_ZP_Z$ one (2.93 eV) as expected due to the increased crowding and more sizeable P_Z configuration. If we compare the changes in the characteristics of the adsorption mode in the monolayer, we first note that the Ti-N bond length is increased from 2.30 Å (0.25 ML) to 2.37 Å for 1 ML $P_EP_EP_EP_E$ and 2.38-2.39 Å for 1 ML $P_ZP_ZP_ZP_Z$. In addition, at 1ML, there is an interaction between one H atom of the amine group and the surface oxygen atom O2c with a bond length of 2.23 Å. Actually, this NH-O2c bond is not present at 0.25 ML for the same adsorption mode (see Figure 3a). In fact, with increasing coverage, the DAE amine tails are slightly reoriented to point toward the vicinal adsorbed amine end in the same [010] row. This

rotation is associated with a preferential NH—O2c interaction. The projected density of states analysis (PDOS) of the surface before and after adsorption of the DAE ML is reported in the S2 section.

We also considered the formation of a bilayer structure consisting in the *BrBr* mode for two DAE molecules plus two additional DAE molecules in a second layer (not shown); the formation of such configuration is exothermic, with an adsorption energy of ΔE_{ads} = 3.07 eV, less stable than the $P_E P_E P_E P_E$ configuration (ΔE_{ads} = 3.86 eV, i.e. 0.20 eV less per molecule). Figure 7 summarizes all the adsorption energies as a function of coverage for various configurations. The adsorption energy increases linearly with the surface coverage for the P_E configurations (P_E to $P_E P_E P_E P_E$), suggesting that the energy of adsorption per molecule is coverage independent. This could suggest that the interactions between the chains are negligible. However we will demonstrate below that it is not the case. The increase of vdW interactions between the chains in the layer is compensated by the decrease of the chemical Ti-N bond with the surface. From the analysis of all the structures for the various coverage, preferred reaction paths for the monolayer formation can be deduced. At θ=0.25 ML, the DAE molecule (one per cell) chemisorbs in a bridge conformation *Br* with two Ti-N bonds. At 0.5 ML, the *BrBr* structure where all Ti^{4+} atoms are saturated, is isoenergetic with the BrP_Z configuration. For coverage of 0.75 ML, the $BrP_E P_E$ and $P_E P_E P_E$ are also isoenergetic. The full ML is then characterized by a $P_E P_E P_E P_E$ structure. From 0.25 ML to 0.75 ML, in adsorbed configurations where *Br* configurations exist, an increase of the Ti-N bond length is observed from 2.32 Å to 2.43 Å, associated to increasing steric effects causing an energy penalty. The *Br* to *P* transition compensates this energy decrease because the *P* adsorption mode reduces steric hindrance in the adsorbed layer, allowing for a strengthening of Ti-N bonds, as deduced from isoenergetic configurations such as *BrBr* and BrP_Z at 0.5 ML and $BrP_E P_E$ and $P_E P_E P_E$ at 0.75 ML. We thus observe a gradual *Br* to *P* transition with increasing coverage, with intermediate coverage situations where one Ti^{4+} atom is unsaturated, enabling the adsorption of an additional molecule to occur and resulting in the formation of a dense layer.

Adsorption of PPA over the anatase (101) TiO_2 surface

Here the situation is much more simple as each molecule can bind only to one Ti^{4+}center through the amine group. A similar coverage analysis was performed for the PPA molecule to investigate the role of the terminal group in interaction of the molecules with the surface. For

each considered adsorption mode perpendicular to the surface (E or Z configurations), it was found for the most stable configurations that the PPA adsorption energies are close (different by less than 0.30 eV/cell) to the equivalent configuration for the DAE molecule, and thus whatever the surface coverage. For $\theta = 0.25$, the adsorption energies are 1.06 eV and 1.08 eV for the P_E configurations of the DAE and PPA molecules and 1.05 eV and 1.09 eV for the P_Z configurations. At $\theta = 0.5$, the adsorption energies are 1.98 eV and 1.88 eV (P_EP_E mode A) 2.05 eV and 2.06 eV (P_EP_E mode B), 1.50 eV and 1.55 eV (P_ZP_Z mode A), 2.08 eV and 2.06 eV (P_ZP_Z mode B) for the DAE and PPA molecules, respectively. (For more details see Tables SI and SII in the supplementary materials). Moreover, for PPA as for DAE, the P_E conformation is favored from intermediate coverage (0.75 ML, ΔE_{ads}= 2.81 eV for P_E and ΔE_{ads}= 2.50 eV for P_Z) to the ML formation (ΔE_{ads}= 3.55 eV for P_E and (ΔE_{ads}= 2.91 eV for P_Z in Figure 8). For the PPA molecule, from $\theta = 0.25$ to 1, the Ti-N bond length increases from 2.30 Å to 2.37 Å (both in the E and Z conformations) as in the case of the DAE molecule, showing that no electronic inductive effects take place in the DAE compared to PPA. At 0.25 ML, the amine H atom points in the direction to surface O2cfor PPA and DAE whereas at 1ML a reorientation of the amine H atoms towards a vicinal amine and a surface O atom is observed for PPA. Finally, in the most stable configuration of adsorption ($P_EP_EP_EP_E$), the formation of a monolayer of DAE is 0.30 eV more exothermic/cell than the formation of a PPA monolayer (3.86 eV *vs*. 3.55 eV for DAE and PPA respectively), due to a stronger Ti-N chemical bond in the DAE layer (29 % *vs*. 39 % of the total energy of adsorption is due to chemical bonding for PPA and DAE respectively).

Kohn-Sham versus van der Waals contributions in the monolayer formation

The following paragraph focuses on Figure 9 where Kohn-Sham (Cov) and Dispersive (both intermolecular interactions in the layer (Coh) and interfacial substrate/layer adhesive energy (Adh)) contributions of adsorbed configurations of DAE molecules as a function of coverage are detailed. It is worth to note that, for all the investigated structures, dispersion energy (Coh + Adh) accounts for 42 % (P_E) to 100 % ($P_ZP_ZP_ZP_Z$) of the total stabilization energy (*Figure 9 and Tables SIII and SIV in the supplementary materials*).

At 0.25 ML, in the perpendicular *P* orientation and whatever the molecule topology on the surface, a combination of one Ti-N bond, one H-bond (NH-O2c) and 45±2 % van der Waals interactions is obtained. In the *Br* structure, the adsorption energy is enhanced, but surprisingly, without any large increase of the total Kohn-Sham energy (~0.07 eV). This can be partly explained by a compensation in the Kohn-Sham energy between the creation of a

new bond with the surface and the molecule flexibility (see the next section *Ab initio Molecular Dynamics (MD) of the full DAE layer in vacuum)*. Furthermore, in this configuration, Ti-N bond lengths are slightly increased compared to *P* mode. In fact, the energy gain in the bridge structure is brought mainly by the molecule-surface van der Waals interactions, as, obviously, the entire molecule is closer to the surface than in the perpendicular orientation, revealing a contribution to the adsorption energy up to 51 % for vdW interactions.

The activation barriers for the *P* to *Br* transition or *Br* to *P* transition are not large even at high coverage, which explains the ability of the DAE to attach and separate one of its extremities from the surface as a function of the coverage. This ability to change adsorption mode from *Br* to *P* and *vice versa* is intimately coupled to the coverage where dispersive contributions will work in tandem with Kohn Sham contributions: Bridge configuration exhibits steric effects once coverage reaches 0.5 ML. It is noticeable by an increase of the number of Ti-N bonds in both *Br* configurations. These steric effects can then be reduced through a favorable *Br* to *P* transition. Between 0.25 ML and 0.5 ML when *Br* configurations are involved, we observe that the Kohn Sham part of the total energy decreases from 49 % in *Br* to 43 % in *BrBr* (Figure 9) as the Ti-N bonds stretched from 2.37 Å/2.32 Å in *Br* to 2.40 Å/2.35 Å and 2.42Å and 2.35 Å in *BrBr*. For the *Br* to *P* transition, notably in BrP_Z, we observe that Kohn Sham part increases up to 48 %, to finally provide an equivalent total adsorption energy of around 2.50 eV for *BrBr* and BrP_Z configurations. The same conclusions can be drawn for 0.75 ML since three isoenergetic adsorbed configurations are identified, i.e. BrP_ZP_Z, BrP_EP_E and $P_EP_EP_E$: in BrP_ZP_Z Ti-N bonds are weakened (2.43 Å, 2.37 Å for the *Br*-DAE, and 2.39 Å and 2.37 Å) resulting in 28% Kohn-Sham part of the total adsorption energy, whereas the Kohn-Sham contribution is enhanced when conformation changes from BrP_ZP_Z to BrP_EP_E (28% to 47 %). Then, the Br to P transition is also a favorable process to help reducing steric effects encountered in BrP_ZP_Z (44% of Kohn Sham part in $P_EP_EP_E$).

At the full ML coverage, the DAE-P_E monolayer formation has the strongest Kohn-Sham energy (1.47 eV), representing 39 % of the total (DFT-D) adsorption energy (See Figure 9). The other 61 % (2.37 eV) come from the dispersive contribution, that can be decomposed in 2/3 due to the interaction between the surface and the molecules and 1/3 due to molecular interactions energy between the DAE molecules within the monolayer. Similar ratios are found for the PPA-E monolayer coverage.

Adsorptions of both DAE and PPA in Z conformations are less favorable than the adsorption of the E conformations for the densest monolayers. The Kohn-Sham energies are negligible

with an athermic value of -0.06 eV and +0.07 eV respectively. For the Z conformations, the adsorption energies are thus only due to high dispersive contributions: 2.99 eV for DAE-Z and 2.84 eV for PPA-Z. These results highlight that medium scale and long scale dispersive forces can force the adsorption and monolayer formation, even in the presence of short-range steric hindrance.

Ab initio Molecular Dynamics (MD) of the full DAE layer in vacuum

From the DFT results, we undertook an *ab initio* MD study of the most stable ML configuration, i.e. the $P_EP_EP_EP_E$ DAE layer adsorbed on TiO_2. It was found that most of adsorbed DAE molecules retain a linear P_E conformation of the chain along the entire trajectories. Only 13% of the DAE molecules present a stable bended P_Z conformation.

In the monolayer, preferential orientations of the DAE chains with respect to the surface are also observed. In particular, DAE chains are tilted by +20° or -20° with respect to the plane normal to the surface along the [10-1] direction (Figure 10a). This arrangement allows the formation of H-bonds (as detailed below) between the amine group involved in the coordination with the Ti surface atoms and the vicinal oxygen surface atoms. Along the whole trajectory the DAE molecules switches from one orientation to the other one each 3 ps. As presented in Figure 10b, the tilting of the DAE molecules placed on the same [010] row occurs in a concerted way. In contrast, the orientation of vicinal DAE molecules adsorbed on different [010] rows are not correlated, because they are not interacting, and therefore two geometrical arrangements are possible, i.e. DAE molecules on vicinal rows can be tilted in the same or the opposite orientations. During 50% of the simulation time, DAE chains of vicinal [010] rows lie with the same orientation while they lie in opposite orientation for the other 50% of time (see Figure 10b).

H-bond analysis has been conducted to better understand the interaction of the DAE molecules with the surface and the interaction among the DAE molecules of the monolayer (Figure 11a). 50% of the DAE molecules are involved in H-bond interaction with the surface oxygen atoms, whereas negligible H-bonding interaction occurs among the terminal amine groups of the monolayer.

Conclusion

The formation of self assembled monolayers of diaminoethane (DAE) and propylamine (PPA) molecules on anatase (101) TiO_2 surface has been investigated from low coverage to a dense and organized layer. In the case of DAE, the results suggest the following reaction path up to

monolayer formation: at low coverage, molecules form bridge bonds with two surface Ti^{4+} atoms, then at intermediate coverage, a 'bridge to perpendicular' transition of the adsorbed molecules occurs, liberating successively Ti^{4+}atoms, to finally form a full monolayer with all molecules in a perpendicular orientation, with one Ti-N bond per molecule. For the PPA molecule, which exhibits one single NH_2 extremity, adsorption occurs with molecules always perpendicular to the surface (at all coverages). For both molecules, the full ordered monolayer is the most favored configuration with a formation energy of 3.5 eV/cell and 3.8 eV/cell for PPA and DAE respectively. Dispersion forces are essential: VdW interactions contribute deeply into the monolayer formation up to 40 % and 100 % of the total adsorption energy at low coverage and high coverage, respectively. The data in this paper show that the formation of the dense and well-organized SAM involves a compromise between chemical grafting on the surface, and reduction of steric effects all along the assembly process.

Acknowledgements

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Supplementary Materials

Section S1 provides additional energetic data, and section S2 the electronic analysis of 1ML of DAE adsorbed on TiO2. Section S3 the respective contributions of dispersive and ionocovalent forces. Section S4 shows side views of adsorbed configurations at 0.75 ML.

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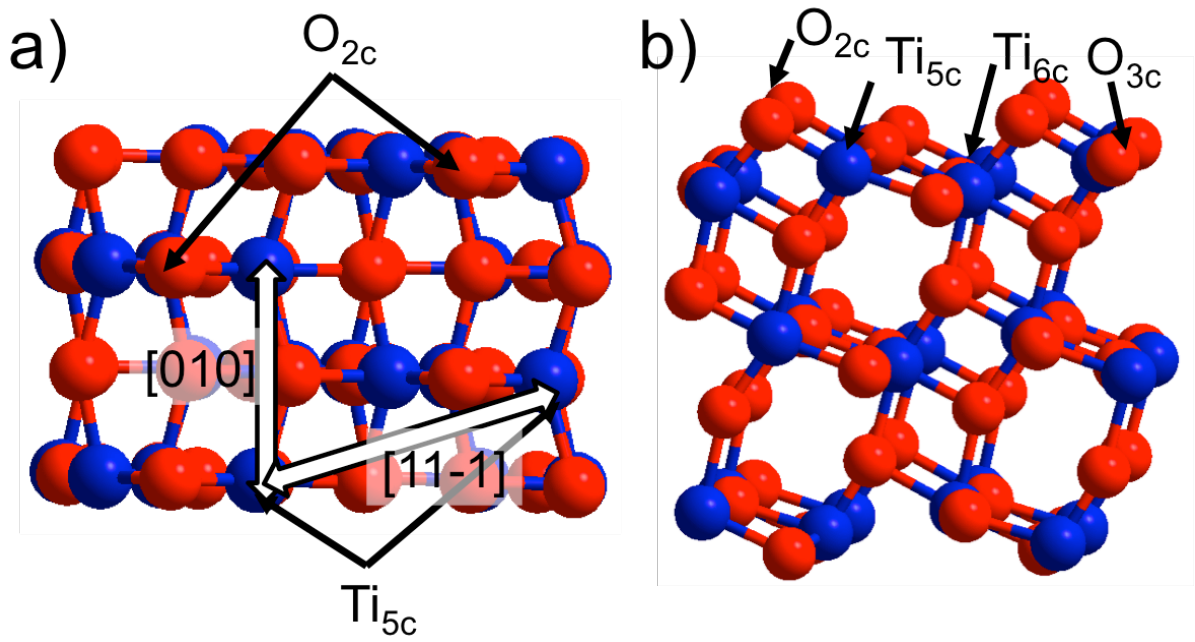


Figure 1.a) Top view and b) Side view of the periodic slab used to model the anatase (101) TiO_2 surface. Covalence of the titanium and oxygen topmost surface atoms and the so-called 'short direction' [010] and 'long direction' [11-1] between Ti^{4+} atoms are shown. Blue and red balls represent titanium and oxygen atoms, respectively. This color scheme is used throughout the paper.

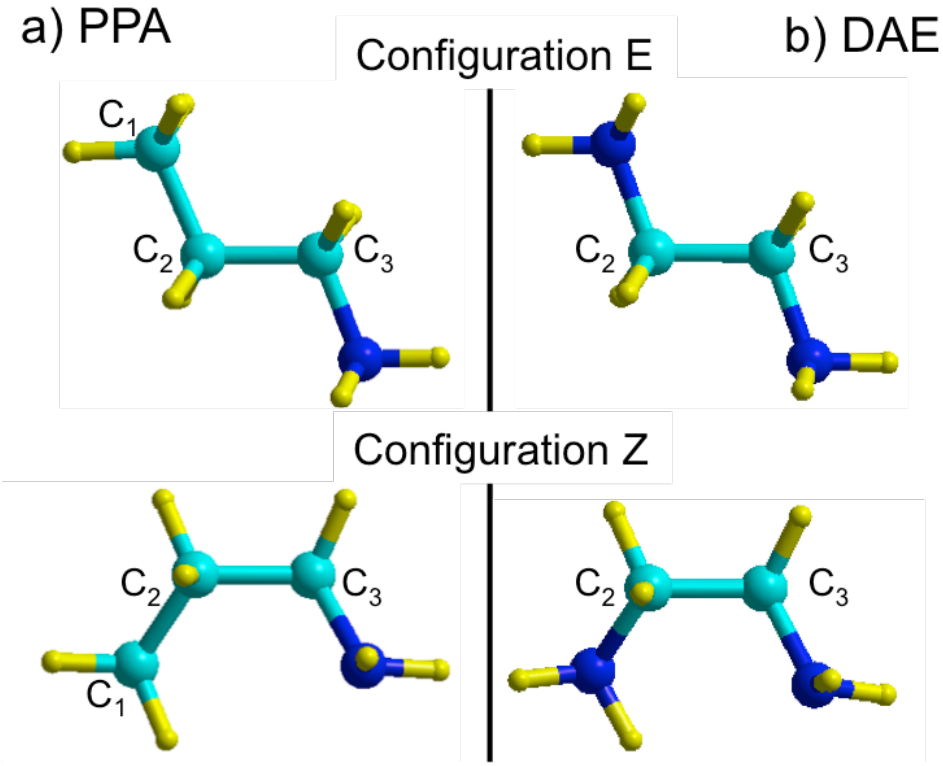


Figure 2. E and Z configurations of a) Propylamine (PPA) and b) Diaminoethane (DAE) molecules. Light blue spheres, dark blue and yellow spheres represent carbon, nitrogen and hydrogen atoms, respectively. This color scheme is used throughout the paper.

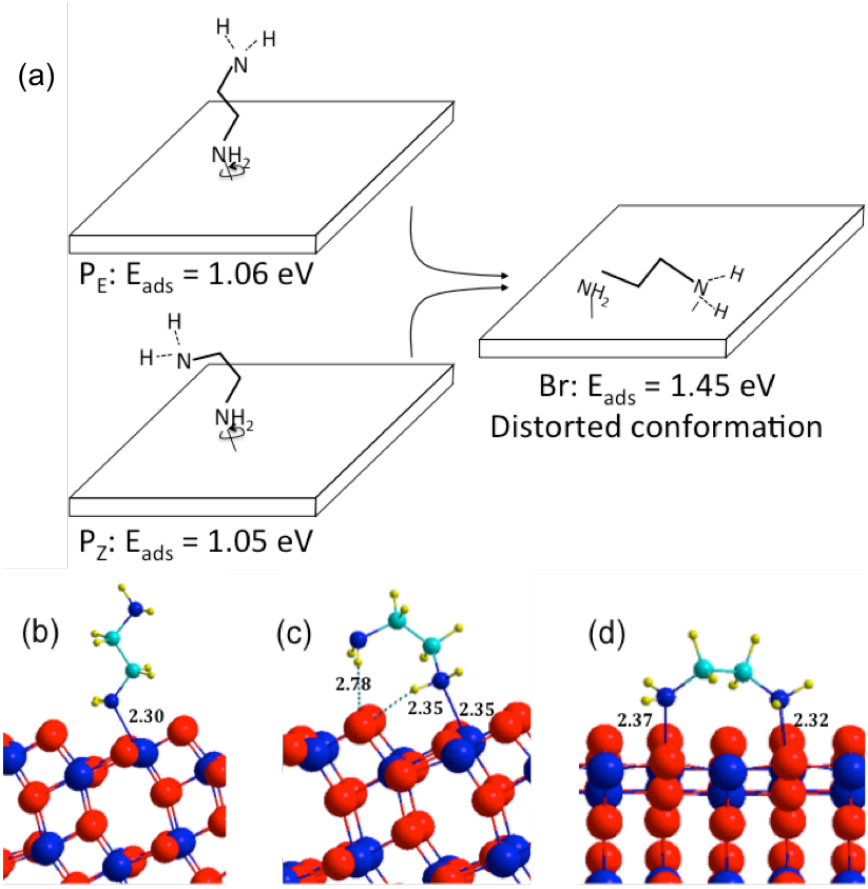


Figure 3. a) Possible orientations of the adsorbed DAE molecule on the dehydrated anatase (101) TiO_2 surface at 0.25 ML. The molecule lies parallel to the [010] direction. b-d) most stable structures. Bond lengths are given in Å.

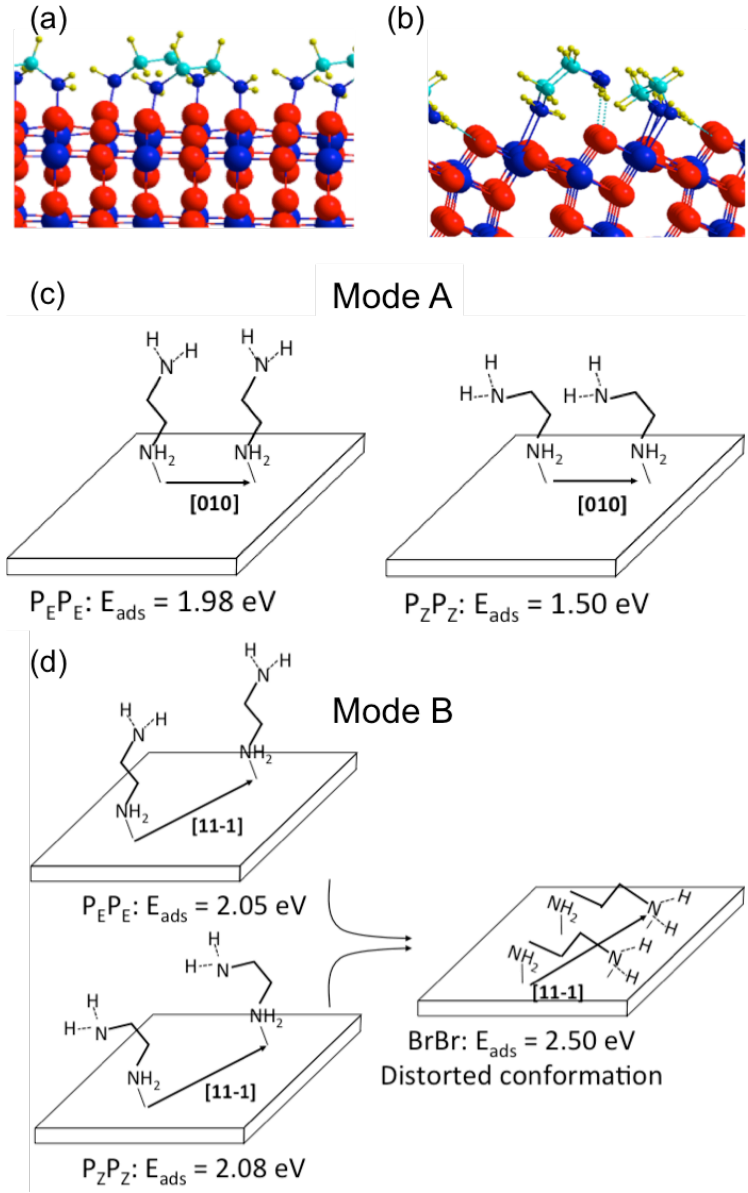


Figure 4. a) and b) Adsorbed configurations at 0.5 ML for isoenergetic *BrBr* and BrP_Z structures, respectively. c) and d) Possible arrangement of DAE molecules on the anatase (101) TiO_2surface at a coverage of 0.5 ML by considering only vertical adsorption *PP* modes (c), and path from perpendicular to parallel configurations (d), Mode A and mode B are significant of DAE molecules aligned in [010] and [11-1] directions respectively.

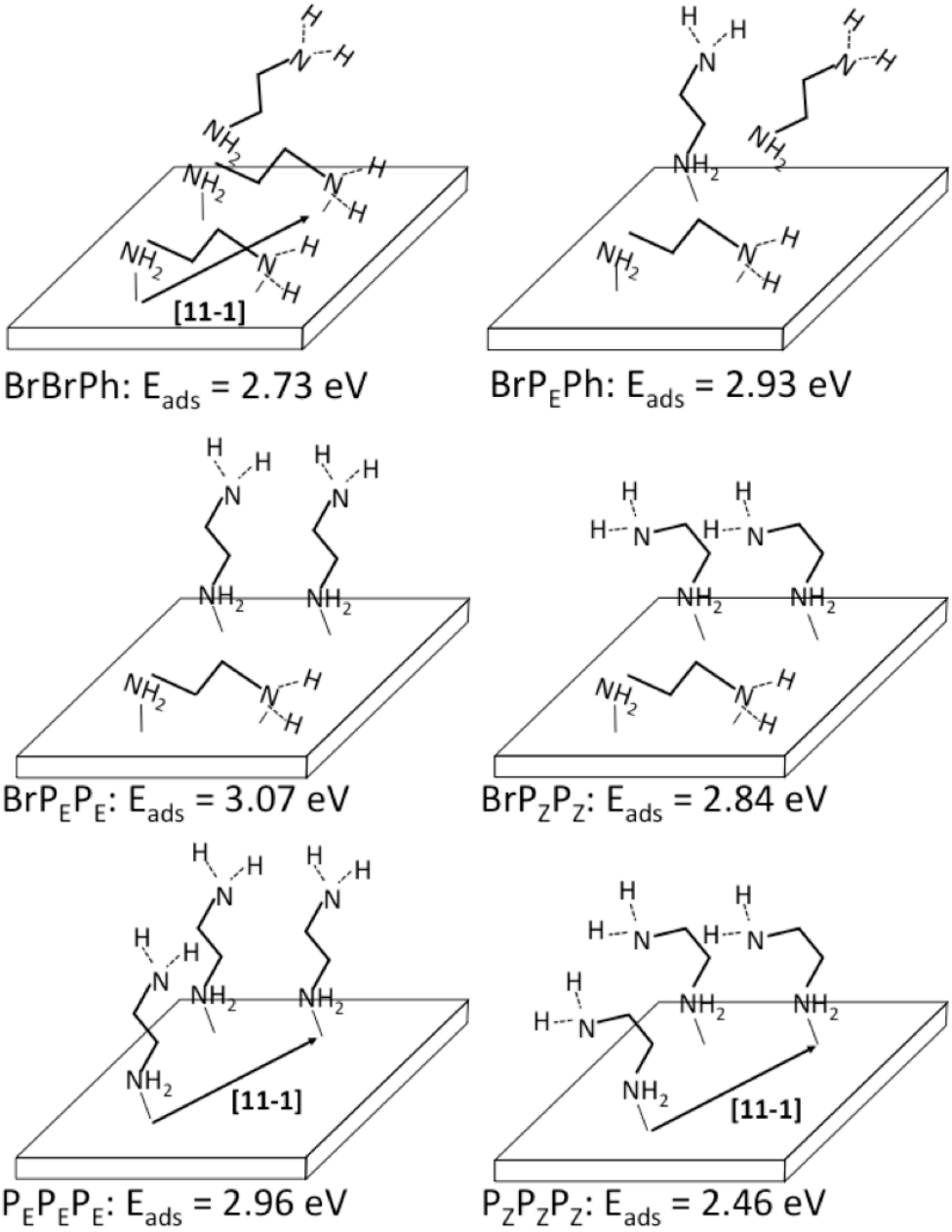


Figure 5. Possible arrangements for DAE molecules on the anatase (101) TiO_2surface at coverage of 0.75 ML.

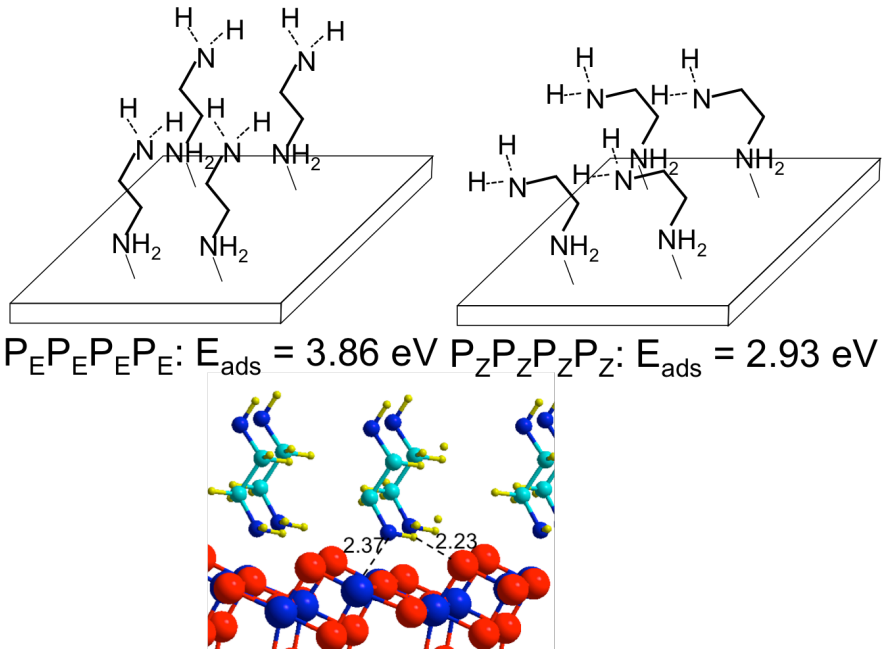


Figure 6. Possible configurations of DAE molecules on the anatase (101) TiO_2 surface at coverage of 1 ML. Relaxed configuration of the most stable structure $P_EP_EP_EP_E$ is given. Bond lengths are in Å.

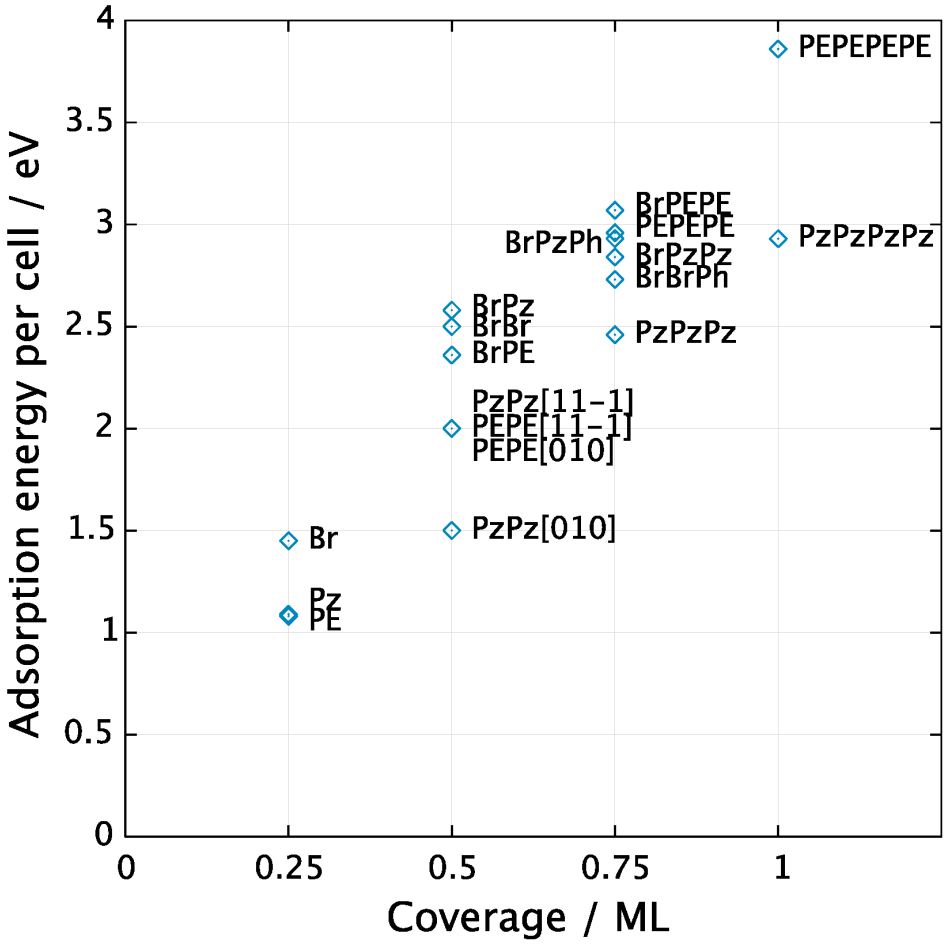


Figure 7. Adsorption energy (eV) versus coverage for adsorption of DAE on the anatase (101) TiO_2 surface as a function of the surface coverage with various configurations of adsorbed molecules (P_E, Pz, Br, Ph).

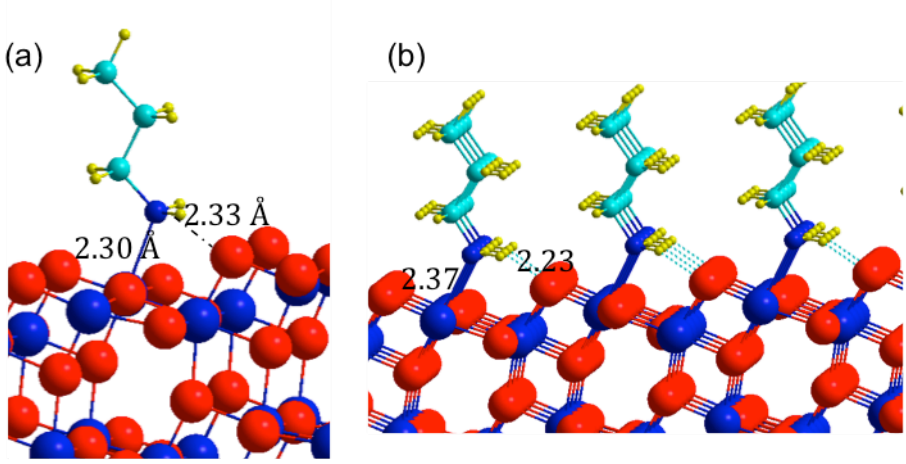


Figure 8. Most stable configurations obtained for PPA adsorbed on anatase (101) TiO_2 surface at a) 0.25 ML and b) 1 ML. Bond lengths are given in Å.

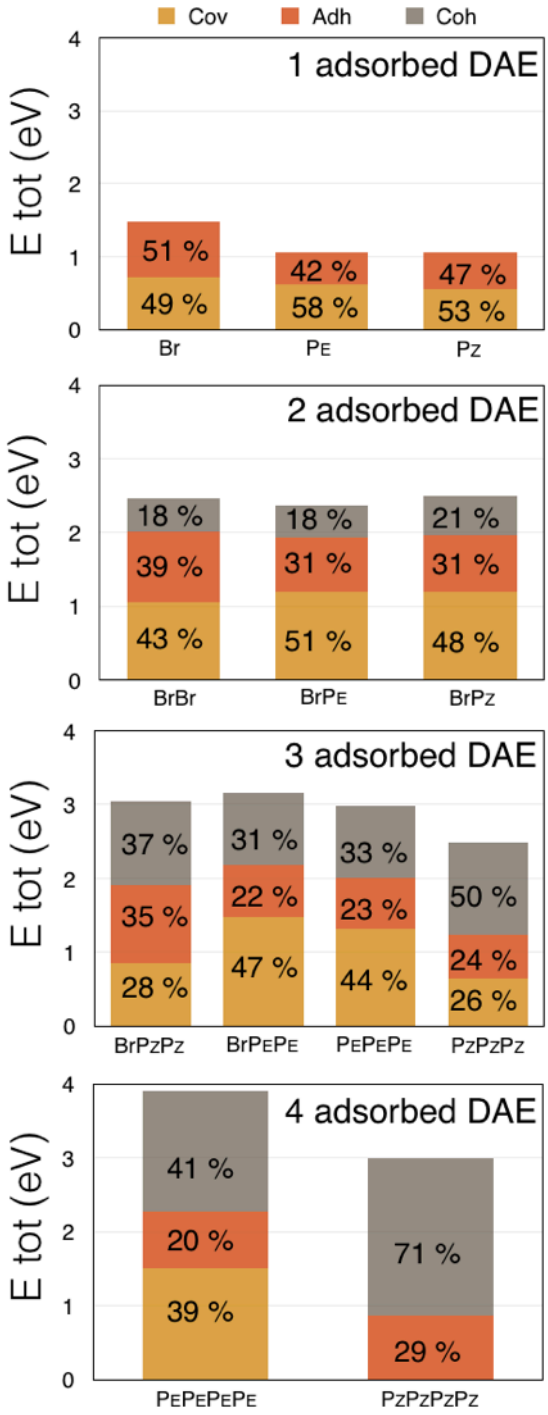


Figure 9. Kohn Sham and dispersive contributions obtained for the adsorption of DAE as a function of coverage. Only selected adsorbed configurations are described. The yellow area represents the DFT contribution depicted as Kohn Sham part (Cov). Orange area represents the dispersive contribution (D) due to the interaction energy between the surface and the molecules (Adh). Grey area is the cohesive energy between molecules contributing to the dispersive forces (Coh). Percent of each contribution of the total adsorption energy of each configuration is provided.

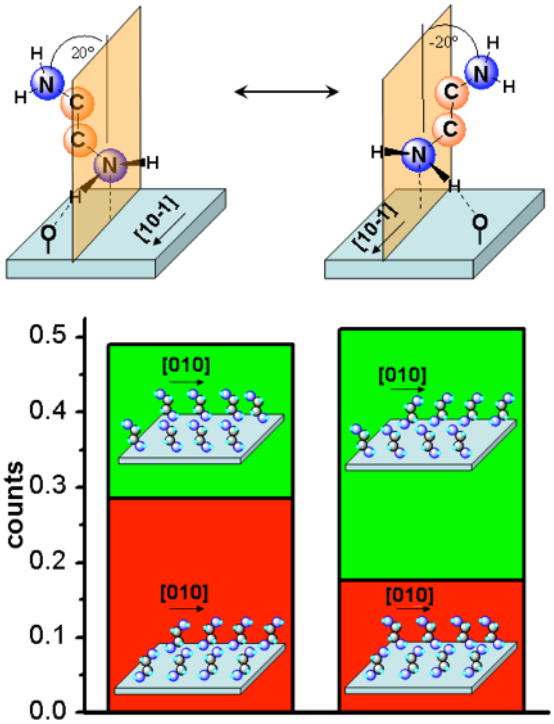


Figure 10. a) Preferential orientation of the DAE chain with respect to the surface. b) Distribution of the preferred orientations of the DAE molecules placed in vicinal [010] rows.

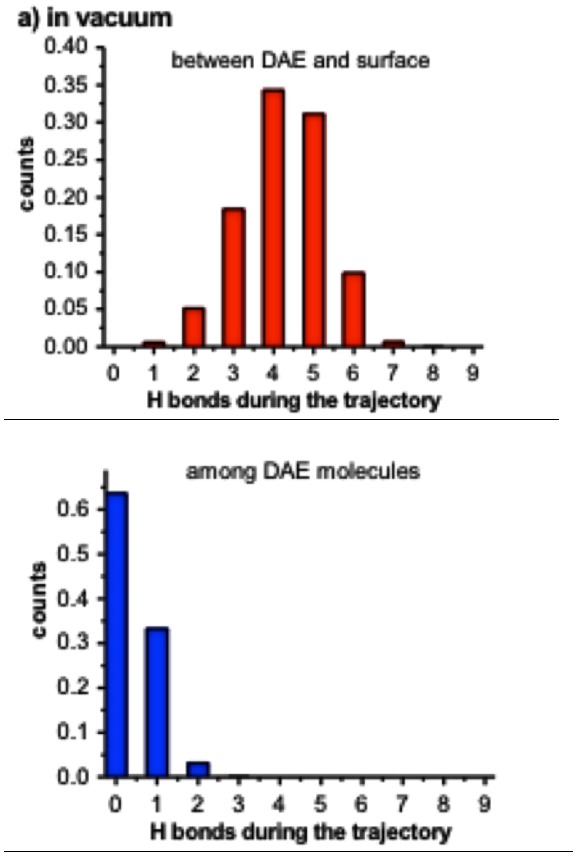


Figure 11. H bonds analysis at the DAE/TiO_2 interface in vacuum. Counts refer to the percentage of time in which n H-bonds are counted.

Supplementary materials

S1: Energetics details

Table SI. Adsorption energy (eV) of an amine DAE or PPA molecule (0.25ML) on the anatase (101) TiO_2 surface calculated using DFT-D method. Negligible differences in the energetic trends are found among the analyzed configurations, except for the PPA along the long direction.

Eads (eV)	Molecule bent towards the [11-1] direction	Molecule bent towards the [010] direction	Molecule⊥to the surface
DAE_P_E	1.04	1.01	1.06
DAE_P_Z	1.05	1.05	1.05
PPA_P_E	0.88	1.03	1.08
PPA_P_Z	0.89	1.09	1.09

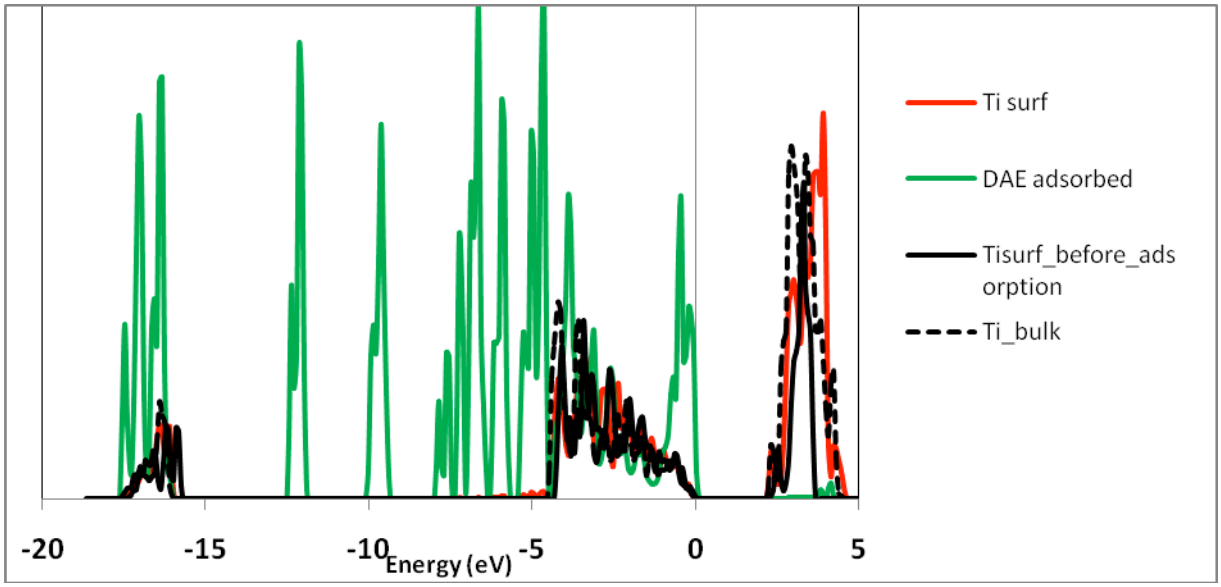
Table SII. DFT-D total adsorption energies relative to DAE-P_E, DAE-P_Z, PPA-P_E and PPA-P_Z in the perpendicular mode of adsorption, on anatase (101) TiO_2 surface as a function of the molecule coverage. Energy values are given in eV. Mode A and B refer to Figure 5: mode A = molecules adsorbed on vicinal sites along a [010] row, mode B = molecules adsorbed on vicinal sites along a [11-1] row.

Coverage (ML)	0.25 ML	0.5 ML		0.75 ML	1 ML
		Mode A	Mode B		
DAE_P_E	1.06	1.98	2.05	2.96	3.86
DAE_P_Z	1.05	1.50	2.08	2.46	2.93
PPA_P_E	1.08	1.88	2.06	2.81	3.55
PPA_P_Z	1.09	1.55	2.06	2.50	2.91

S2: Electronics Analysis

The Figure reports the analysis of the density of states of the TiO_2 slab before and after DAE adsorption (one ML coverage). First, the calculated band gap in bulk anatase was 3.2 eV, in good agreement with experimental values [1]. Then, we notice that Ti surface atoms electronic states are identical to the bulk, without and with adsorption. Finally, the electronic levels of the adsorbed DAE are aligned with that of the Ti surface atoms. The band at the Fermi level is composed of N 2p states, and the slight overlap with the Ti 3p states indicates that the

bonding has a partially covalent character. The same trend was observed at low coverage (alignment of the N 2p state with the surface Ti 3p state).



S3: Kohn-Sham versus dispersive contributions to adsorption

Table *SIII*: *Kohn-Sham* and dispersive contributions in the adsorption energy (eV) of an amine molecule ($\theta = 0.25$) on the anatase (101) TiO_2 surface.

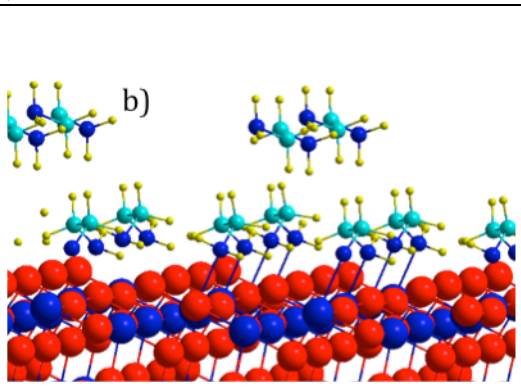
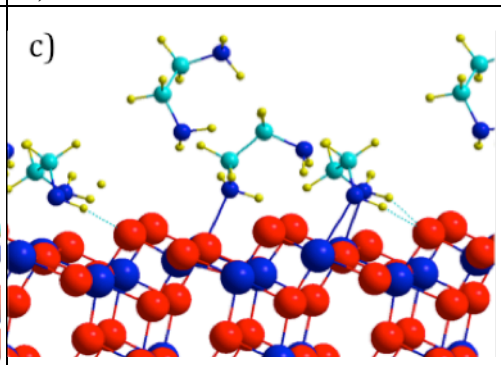
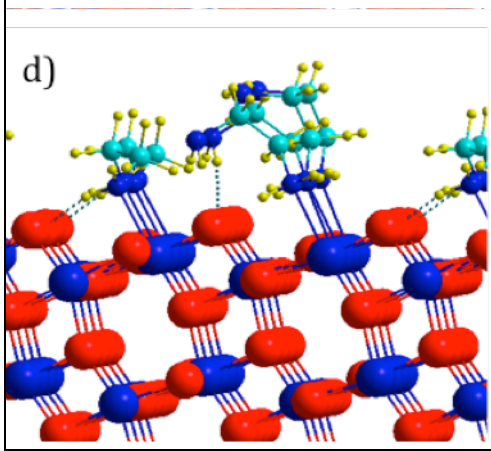
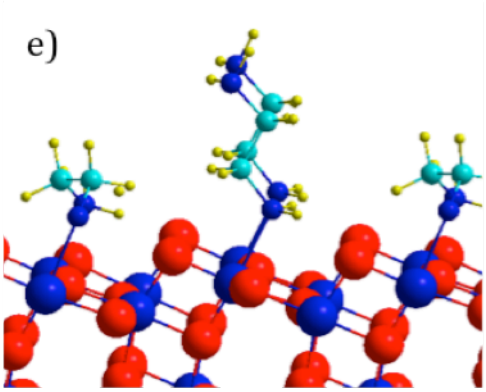
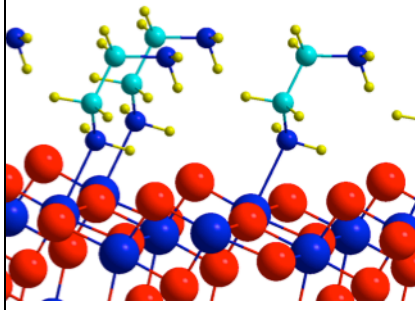
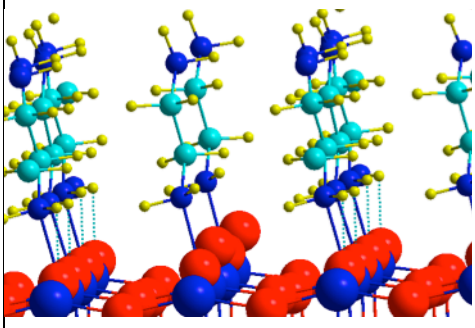
Eads (eV)	DFT	D	DFT-D
DAE_P_E	0.62	0.37	1.06
DAE_P_Z	0.56	0.40	1.05
PPA_P_E	0.70	0.38	1.08
PPA_P_Z	0.69	0.40	1.09

Table *SIV*: Kohn-Sham and dispersive contributions in the adsorption energy (eV) of four amines molecules ($\theta = 1$) on the anatase (101) TiO_2 surface. These values refer to Figure 9.

Eads / ML (eV)	DFT	D	DFT-D
DAE_P_E	1.47	2.37	3.86
DAE_P_Z	-0.06	2.99	2.93
PPA_P_E	1.02	2.53	3.55
PPA_P_Z	0.07	2.84	2.91

S4: Coverage θ = 0.75

Figure. Possible DAE molecules configurations on the anatase (101) TiO_2 surface at a coverage of 0.75 ML, (adsorption energy in eV) and possible pathway for the bridge to perpendicular transition.

a)	b)
	
BrBrPh 2.73 eV	BrPEPh 2.93 eV
c)	d)
	
BrPzPz 2.84 eV	BrPEPE 3.07 eV
e)	f)
	
PzPzPz 2.46 eV	PEPEPE 2.96 eV