Supporting Information

for

Understanding the topography effects on competitive adsorption on a nanosized anatase crystal: a molecular dynamics study.

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Table of Contents

(00-1) Anatase surface exposing bridging oxygens connected to titanium atoms

Ideal anatase crystal surface: quinoline at small concentration

In the dyn_CRY_40mol_5ns.avi, the molecules that are adsorbed on the (001) crystal face at the beginning of the MD run are shown in green. These weakly interacting molecules migrate on all the other faces during the MD run.

Ideal anatase crystal surface: quinoline at small concentration after removing some molecules

Ideal anatase crystal surface: quinoline at large concentration

In the dyn_CRY_300mol_5ns.avi, the molecules that are adsorbed on the (001) crystal face at the beginning of the MD run are shown in green. Also in this MD run, these weakly interacting molecules migrate on all the other faces.

Ideal anatase crystal surface: quinoline at large concentration after removing the molecules from three (100) surfaces considering the geometry optimized after the MD run at large concentration

In the dyn_CRY_182mol_5ns.avi, the molecules that initially are adsorbed on the (00-1) crystal face at the beginning of the MD run are shown in green. Some of these molecules migrate on the bare (100) faces during the MD run.

(001) Anatase surface exposing -OH groups

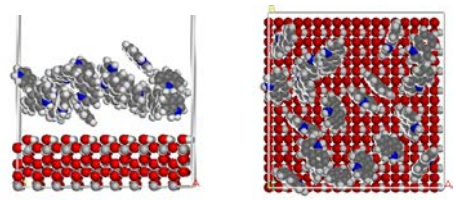


Fig. S1.a1 Initial *non-optimized* geometry of quinoline molecules at small concentration (20 molecules) near the (001) anatase surface, side and top view.

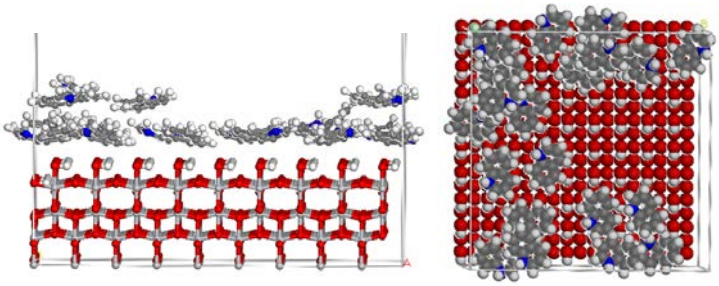


Fig. S1.a2 Initial ***optimized*** geometry of quinoline molecules at small concentration near the (001) anatase surface, side and top view.

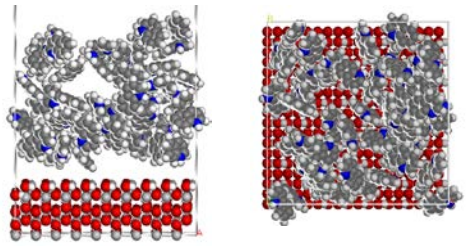


Fig. S1.b Initial *non-optimized* geometry of quinoline molecules at large concentration (50 molecules) near the (001) anatase surface, side and top view.

The geometry/orientation on the single (001) anatase surface exposing –OH groups, present quinoline molecules at small and at large concentration *randomly disposed* parallel to the surface both in the initial interaction stage (see *for example* Fig. S.1.a2) and in the final adsorption geometry. The results obtained after the MD run and energy minimization are reported in the article in Fig.3 and commented below.
In this case only at large concentration a total coverage of the surface is observed.

In presence of competitive adsorption on the anatase nanocrystal, we observe that all the quinoline molecules weakly interacting after initial optimization and *randomly disposed* parallel to this face, migrate after the MD run to the other neighboring surfaces, in order to better interact as discuss in the article.

(100) Anatase surface exposing bridging oxygens connected to titanium atoms

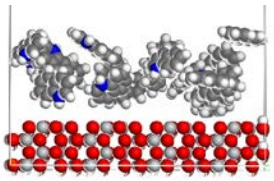


Fig. S2.a1 Initial *non-optimized* geometry of quinoline molecules at small concentration (20 molecules) near the (100) anatase surface, side view.

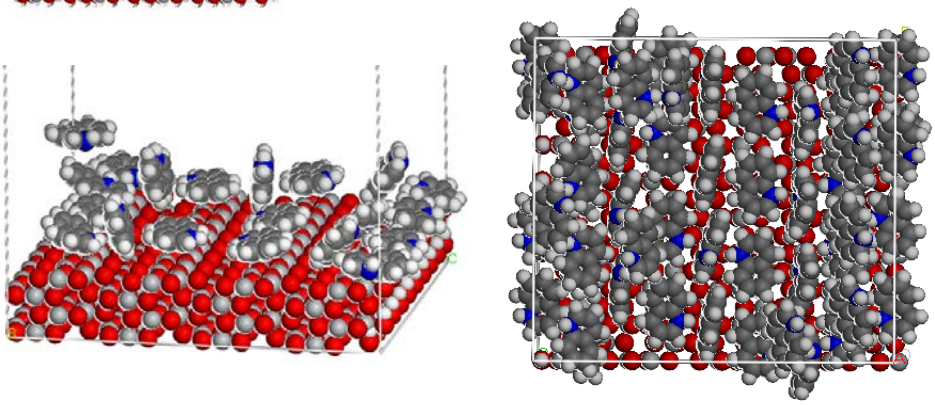


Fig. S2.a2 Initial ***optimized*** geometry of quinoline molecules at small concentration (20 molecules) near the (00-1) anatase surface, side view and top view.

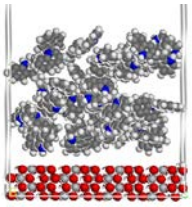


Fig. S2.b1 Initial *non-optimized* geometry of quinoline molecules at large concentration (50 molecules) near the (100) anatase surface, side view.

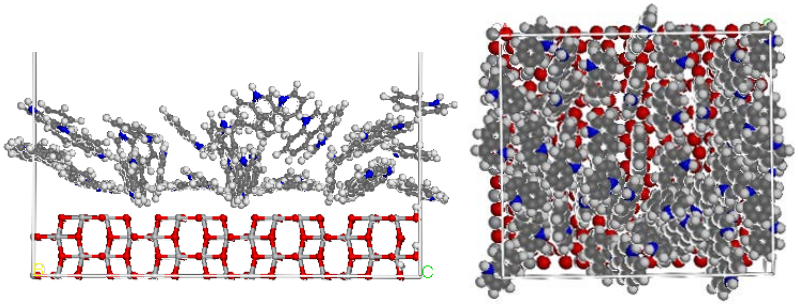


Fig. S2.b2 Initial ***optimized*** geometry of quinoline molecules at large concentration (50 molecules) near the (100) anatase surface, side and top view.

The geometry/orientation on the single (100) anatase surface exposing bridging oxygens connected to titanium atoms present quinoline molecules at small and at large concentration *ordered* parallel and perpendicular to the surface, both in the initial (see Fig. S.3.a2 and S.3.b2) and in the final adsorption geometry. The results obtained after the MD run and energy minimization are reported in the article in Fig.3 and commented below.
In this particular case studied both at small and at large concentration a total coverage of the surface is observed.

In presence of competitive adsorption on the anatase nanocrystal, we always observe coverage of this surface. The geometry interaction present molecules *ordered* parallel and perpendicular to the surface. The first layer is always more ordered, preferentially with the nitrogen atoms toward to surface.

(00-1) Anatase surface exposing bridging oxygens connected to titanium atoms

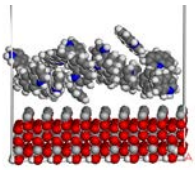


Fig. S3.a1 Initial *non-optimized* geometry of quinoline molecules at small concentration (20 molecules) near the (00-1) anatase surface, side view.

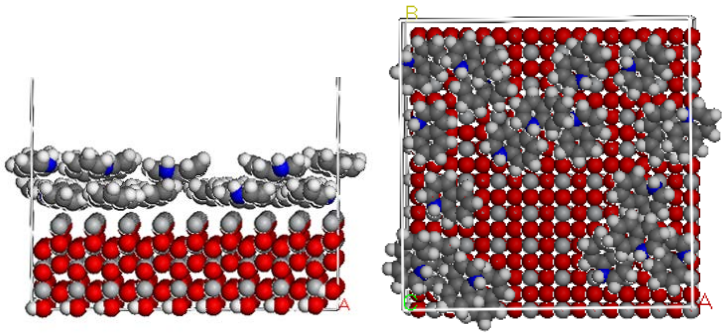


Fig. S3.a2 Initial ***optimized*** geometry of quinoline molecules at small concentration (20 molecules) near the (00-1) anatase surface, side and top view.

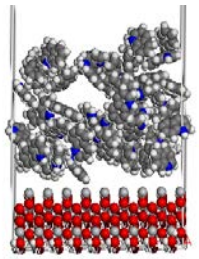


Fig. S3.b1 Initial *non-optimized* geometry of quinoline molecules at large concentration (50 molecules) near the (00-1) anatase surface, side view.

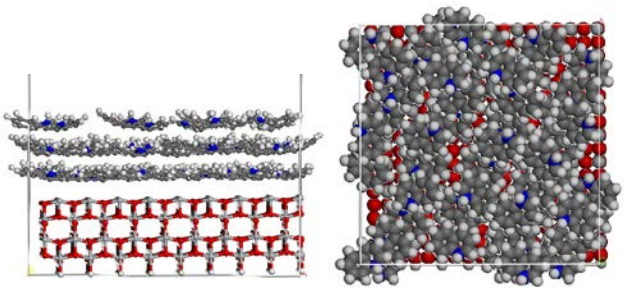


Fig. S3.b2 Initial *non-optimized* geometry of quinoline molecules al large concentration (50 molecules) near the (00-1) anatase surface, side and top view.

The geometry/orientation on the single (00-1) anatase surface exposing bridging titanium atoms present quinoline molecules at small and at large concentration *randomly disposed* parallel to the surface, both in the initial (see Fig. S.2.a2 and S.2.b2) and in the final adsorption geometry. The results obtained after the MD run and energy minimization are reported in the article in Fig.3 and commented below.
Also in this case only at large concentration a total coverage of the surface is observed.

In presence of competitive adsorption on the anatase nanocrystal, we observe that quinoline molecules strongly interacting with this crystal face form one or more layers of molecules *randomly disposed* parallel to the surface depending of the concentration.

Ideal anatase crystal surface: quinoline at small concentration

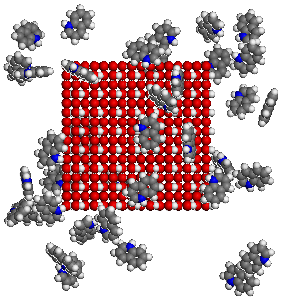
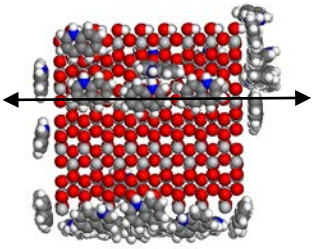
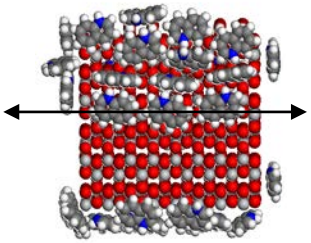


Fig. S4.a Initial *non-optimized* geometry of quinoline molecules at small concentration (40 molecules) near the ideal anatase crystal, within a cubic cell of 150 Å with periodic boundary conditions.

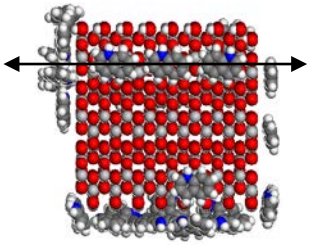
Face 1 (100)



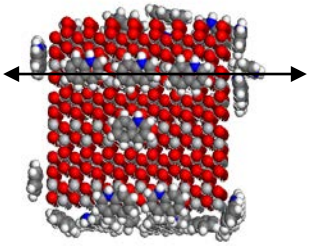
Face 2 (100)



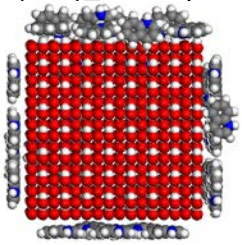
Face 3 (100)



Face 4 (100)



Face 5 (001)_OH exposed at the surface



Face 6 (00-1)_ Ti exposed

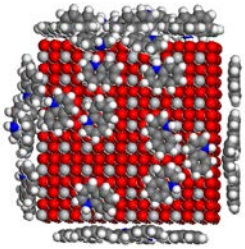


Fig. S4.b The final adsorption geometry of quinoline ***optimized*** after a 5 ns MD run at room temperature of the initial arrangement shown above in Fig. S4.a (the legends indicate the specific face viewed from above).

Note that a small concentration the quinoline molecules adsorbed on the four (100) surfaces are mostly parallel to the surfaces, while very few molecules are perpendicular. Considering the long axis of the quinoline molecule, the nitrogen atoms are arranged on the same side.

After the MD run and energy minimization, there are no molecules adsorbed on the (001) surface; on the (00-1) surface, the molecules are randomly disposed parallel to the surface, as reported in Fig. S4b.

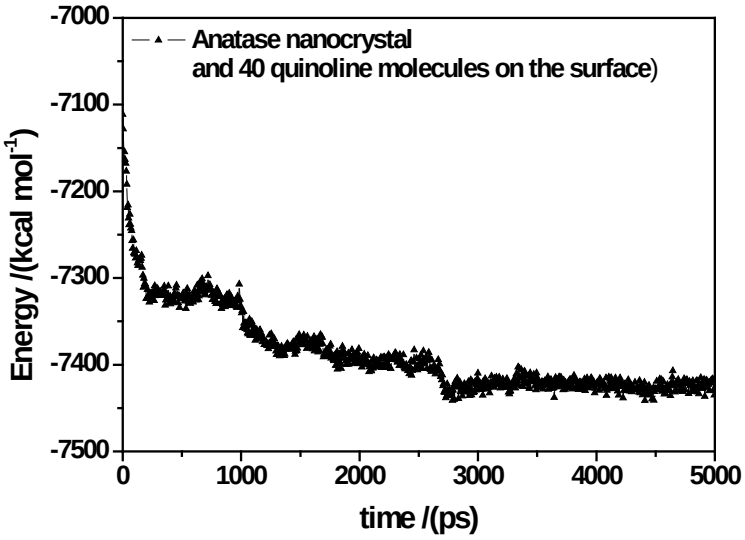


Fig. S4.c Total energy (kcal mol^{-1}) plotted as a function of time t (ps).

In the dyn_CRY_40mol_5ns.avi, the molecules that are adsorbed on the (001) crystal face at the beginning of the MD run are shown in green.

Ideal anatase crystal surface: quinoline at small concentration after removing the molecules from three (100) surfaces considering the geometry optimized after the MD run at small concentration

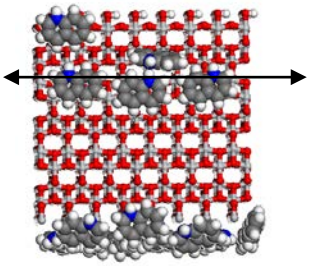
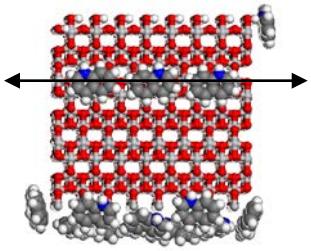
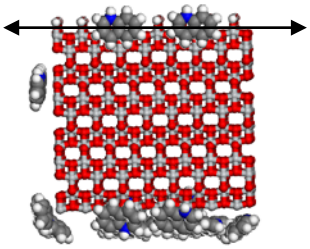


Fig. S5.a Initial *non-optimized* geometry of quinoline molecules at small concentration (20 molecules) near the ideal anatase crystal, within a cubic cell of 150 Å with periodic boundary conditions, obtained after removing 20 molecules adsorbed on three (100) faces.

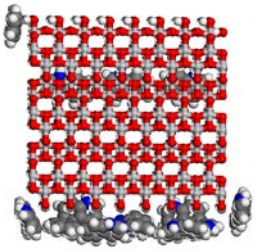
Face 1 (100)



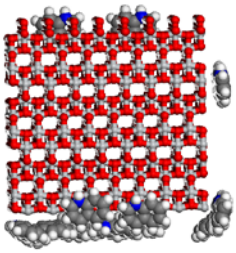
Face 2 (100)



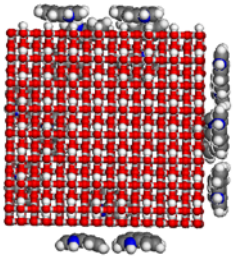
Face 3 (100)



Face 4 (100)



Face 5 (001)_OH exposed at the surface



Face 6 (00-1)_ Ti exposed

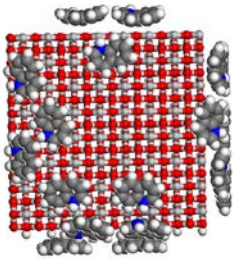


Fig. S5.b The final adsorption geometry of quinoline molecules ***optimized*** after a 5 ns MD run at room temperature of the initial arrangement shown above in Fig. S5.a (the legends indicate the specific face viewed from above).

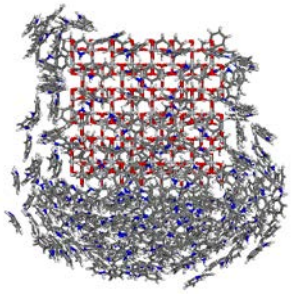
Note that the quinoline adsorbed on the four (100) faces are parallel to the surface and considering the long axis of the molecule, the nitrogen atoms are arranged on the same side. At this small concentration there aren't molecules perpendicular to the (100) surface.

After the MD run and energy minimization no molecules are adsorbed in the (001) surface and on the (00-1) surface they are randomly disposed parallel to the surface, as previously found.
The molecules initially present on one (100) surface migrate on the other surfaces.

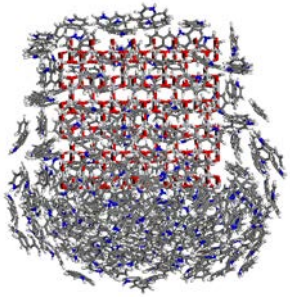
Ideal anatase crystal surface: quinoline at large concentration

Fig. S6.a Initial *non-optimized* geometry of quinoline molecules at large concentration (291 molecules) near the ideal anatase crystal, within a cubic cell of 150 Å (outlined in the Figure) with periodic boundary conditions.

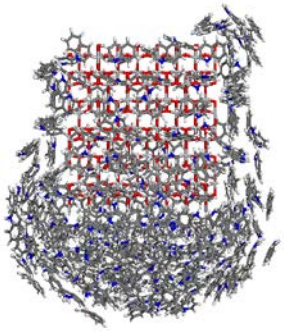
Face 1 (100)



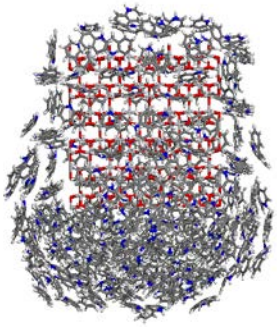
Face 2 (100)



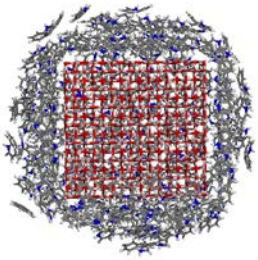
Face 3 (100)



Face 4 (100)



Face 5 (001)_OH exposed at the surface



Face 6 (00-1)_ Ti exposed

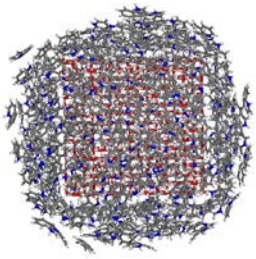


Fig. S6.b The final adsorption geometry of quinoline molecules ***optimized*** after a 5 ns MD run at room temperature of the initial arrangement shown above in Fig. S6.a (the legends indicate the specific face viewed from above).

Note that on the nanosized crystal at large concentration, the molecules adsorbed on the (00-1) face form layers with quinoline randomly disposed parallel to the surface thanks to the strong interaction; on the (100) face they are more ordered, parallel and perpendicular to the surface, as previously found.

After the MD run and energy minimization there aren't molecules adsorbed on the (001), the surface more weakly interacting with quinoline.

In the dyn_CRY_300mol_5ns.avi, the molecules that are adsorbed on the (001) crystal face at the beginning of the MD run are shown in green.

Ideal anatase crystal surface: quinoline at large concentration after removing the molecules from three (100) surfaces considering the geometry optimized after the MD run at large concentration

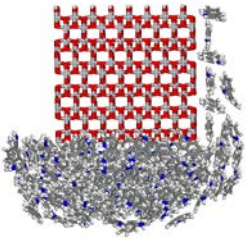
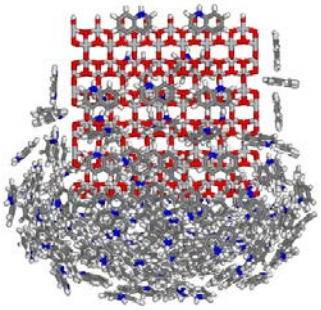
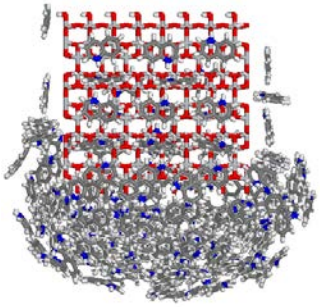


Fig. S7.a Initial *non-optimized* geometry of quinoline molecules at large concentration (291 molecules) near the ideal anatase crystal, within a cubic cell of 150 Å with periodic boundary conditions obtained after removing about 100 molecules adsorbed on three (100) faces of the nanocrystal (182 molecules were considered).

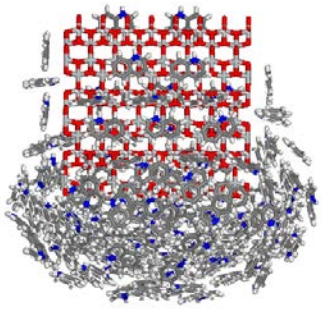
Face 1 (100)



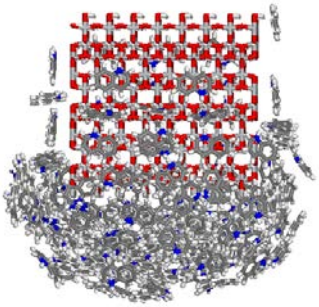
Face 2 (100)



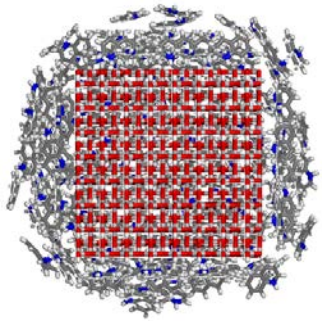
Face 3 (100)



Face 4 (100)



Face 5 (001)_OH exposed at the surface



Face 6 (00-1)_ Ti exposed

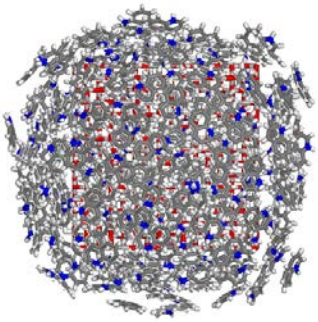


Fig. S7.b The final adsorption geometry of quinoline molecules ***optimized*** after a 5 ns MD run at room temperature of the initial arrangement shown above in Fig. S7.a (the legends indicate the specific face viewed from above).

Note that removing molecules initially adsorbed on three (100) faces, some quinoline migrate from the other surfaces, namely (00-1) and the fourth (100), in order to better interact with the three bare (100) faces, where they are ordered parallel and perpendicular to the surface as already found.
After the MD run and energy minimization there aren't molecules adsorbed on the (001).

In the dyn_CRY_182mol_5ns.avi, the molecules that are adsorbed on the (00-1) crystal face at the beginning of the MD run are shown in green.