Electronic Supplementary Information (ESI)

Corrosion protection of Al(111) by 8-hydroxyquinoline: a comprehensive DFT study

Dimer adsorption

We tested additional initial geometries including the adsorption of dimer assemblies of 8HQ molecules. The optimized geometries are presented in Figure 1.

We calculated the total adsorption energy of the dimer, the adsorption energy per 8HQ molecule and the binding energy.

$$E_{ads/dimer} = E_{slab+dimer} - E_{slab/opt} - E_{freedimer/opt} \tag{1}$$

$$E_{ads/8HQmolecule} = E_{ads/dimer}/2 \tag{2}$$

$$E_{bind/8HQmolecule} = E_{slab+dimer} - E_{slab/sp} - E_{dimer-layer/sp} \tag{3}$$

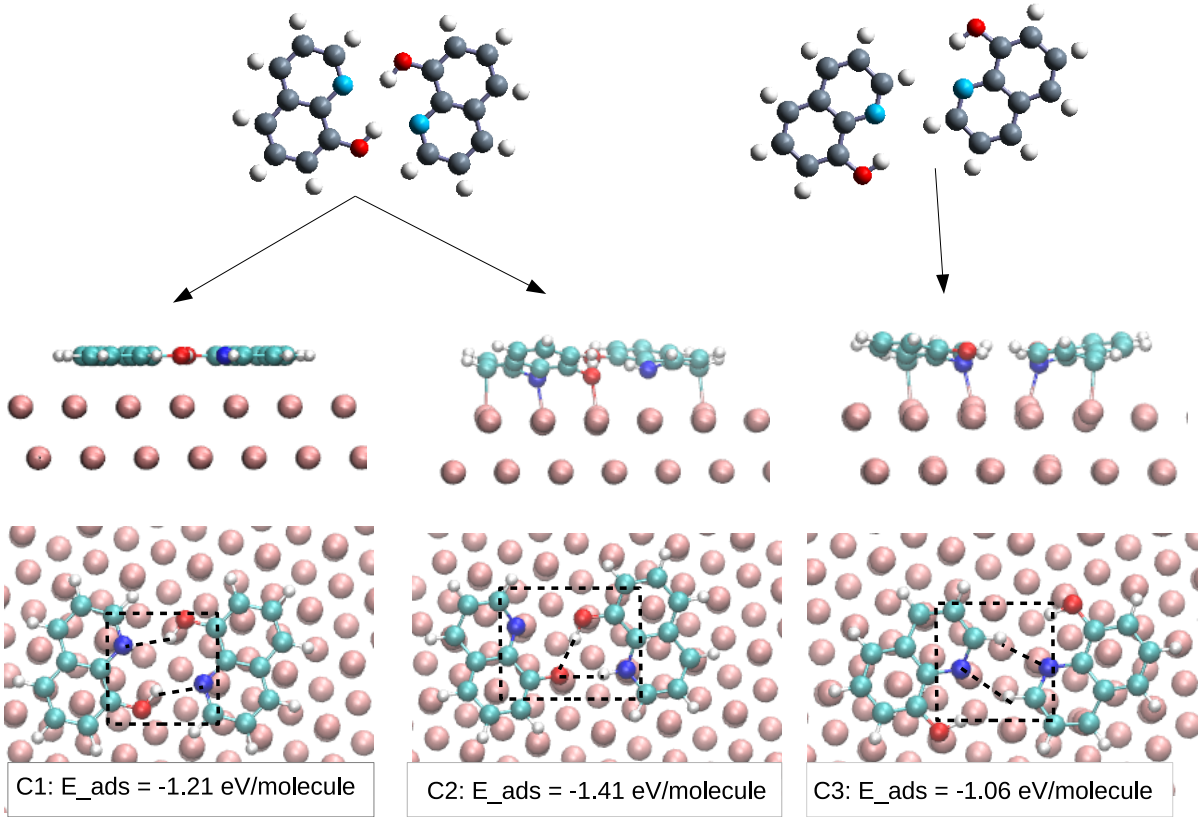

Figure 1: Adsorption topologies of dimer assemblies of 8HQ molecules on Al(111)Left: conformation C1. Middle: conformation C2. Right: conformationC3.

Where $E_{slab+dimer}$ is the total energy of the system with the dimer molecule adsorbed on the Al(111) surface, $E_{slab/opt}$ is the energy of the bare relaxed Al(111) slab calculated without dispersive corrections and $E_{freedimer/opt}$ is the energy of the free dimer optimized in vacuum, $E_{slab/sp}$ and $E_{dimer-layer/sp}$ are the total energies of the isolated slab and isolated deformed dimer layer at their geometry after adsorption, respectively.

The results are presented in Table 1. χ 8HQ monomer corresponds to the native 8HQ molecule, δ 8HQ monomer to the dehydrogenated species and η 8HQ monomer to the hydrogenated species.

We observed the formation of different H-bonding in the dimer (-OH...N, -OH...O, -NH...O, -CH...N). A physisorbed mode was found (see Figure 1 (C1)). In that case the total adsorption energy $E_{ads/dimer}$ was -2.42 eV for the dimer (taking as the reference the free dimer species) or -1.21 eV/8HQmolecule. The adsorbed dimer geometry is not modified when compared to the free dimer species and $E_{bind/8HQmolecule}$, the binding energy per 8HQ molecule on the Al(111) surface, has a value of -1.21 eV. The 8HQ monomer binds

Table 1: H bond length in Å between the atoms of the 8HQ dimer assemblies after adsorption on Al(111), adsorption and binding energies in eV.

Conformations	H bond length	$E_{ads/dimer}$	$E_{ads/8HQmolecule}$	$E_{bind/8HQmolecule}$
C1 on Al(111)	OH—N: 1.99	-2.42	-1.21	-1.21
C2 on Al(111)	OH—O: 1.78	-2.82	-1.41	/
	NH—O: 1.95			
C3 on Al(111)	CH—N: 2.33	-2.12	-1.06	-2.88
χ 8HQ monomer on Al(111)	/	/	-1.11	-2.90
δ 8HQ monomer on Al(111)	/	/	-3.44	-4.20
η 8HQ monomer on Al(111)	/	/	-1.71	-2.31

stronger to the surface than in the case of the dimer (Binding energy: -2.90 eV/molecule for the 8HQ monomer and -1.21 eV/8HQmolecule when the 8HQ is in the form of the dimer). Others conformations are chemisorbed conformations with the formation of covalent bonds between the molecules and the Al surface atoms. It indicates the strong affinity of the 8HQ molecule with aluminum. Two conformations are shown in Figure 1 (C2) and (C3). The most stable adsorption topology of the dimer on the Al(111) surface led to a chemical modification of the organic species (Figure 1 (C2)): one H atom of the hydroxyl group of one 8HQ molecule is transferred to the other 8HQ molecule. The 8HQ dimer becomes thus one hydrogenated and one dehydrogenated species on Al(111) with conformations of the two molecules on the Al(111) surface similar to the conformation of the dehydrogenated δ and hydrogenated η monomers at low coverage (see Table 1 and also presented in the manuscript) but with H bonding between the two species. The total adsorption energy is -2.82 eV (taking as the reference the free dimer species) or -1.41 eV/molecule if we divide the latter value by the number of monomers in the dimer. In our manuscript, for the adsorption of the monomer species, i.e. adsorption of only one type of species for each calculation, the adsorption energy of the dehydrogenated δ molecules is -3.44 eV/molecule independently of the coverage and the adsorption energy of the hydrogenated species is -1.71 eV/molecule independently of the coverage. So the binding of only one type of species is stronger than the adsorption energy of the same species in the modified dimer (averaged at -1.41 eV per molecule). For the conformation in Figure 1 (C3), the total adsorption energy is -2.12 eV for the dimer (taking as the reference the free dimer species) and then -1.06 eV/molecule, and the binding energy per 8HQ

monomer on the Al(111) is -2.88 eV/molecule. The geometries of the 8HQ molecules in the adsorbed dimer species are the same as the geometry of one 8HQ monomer adsorbed on Al(111). In the work presented in the revised manuscript, the adsorption energy for one 8HQ monomer is about -1.11 eV/molecule independently of the surface coverage. The 8HQ monomer binds slightly stronger to the surface than in the case of the dimer (Binding energy: -2.90 eV/molecule for the 8HQ monomer and -2.88 eV/8HQmolecule when the 8HQ is in the form of the dimer). These results show that the association of the molecules as dimers on the Al(111) surface is thus not favored over the adsorption of monomer species, presented in the article.