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**ELECTRONIC SUPPLEMENTARY INFORMATION**

# TETT-functionalized $TiO_2$ nanoparticles for DOX loading: a quantum mechanical study at the atomic scale.

Martina Datteo[1], Lorenzo Ferraro[1], Gotthard Seifert[2] and Cristiana Di Valentin[1,*]

[1] Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,

via R. Cozzi 55, 20125 Milano Italy.

[2] Technische Universität Dresden, Institut für Theoretische Chemie, D-01062 Dresden, Germany

[*] Corresponding author: cristiana.divalentin@unimib.it

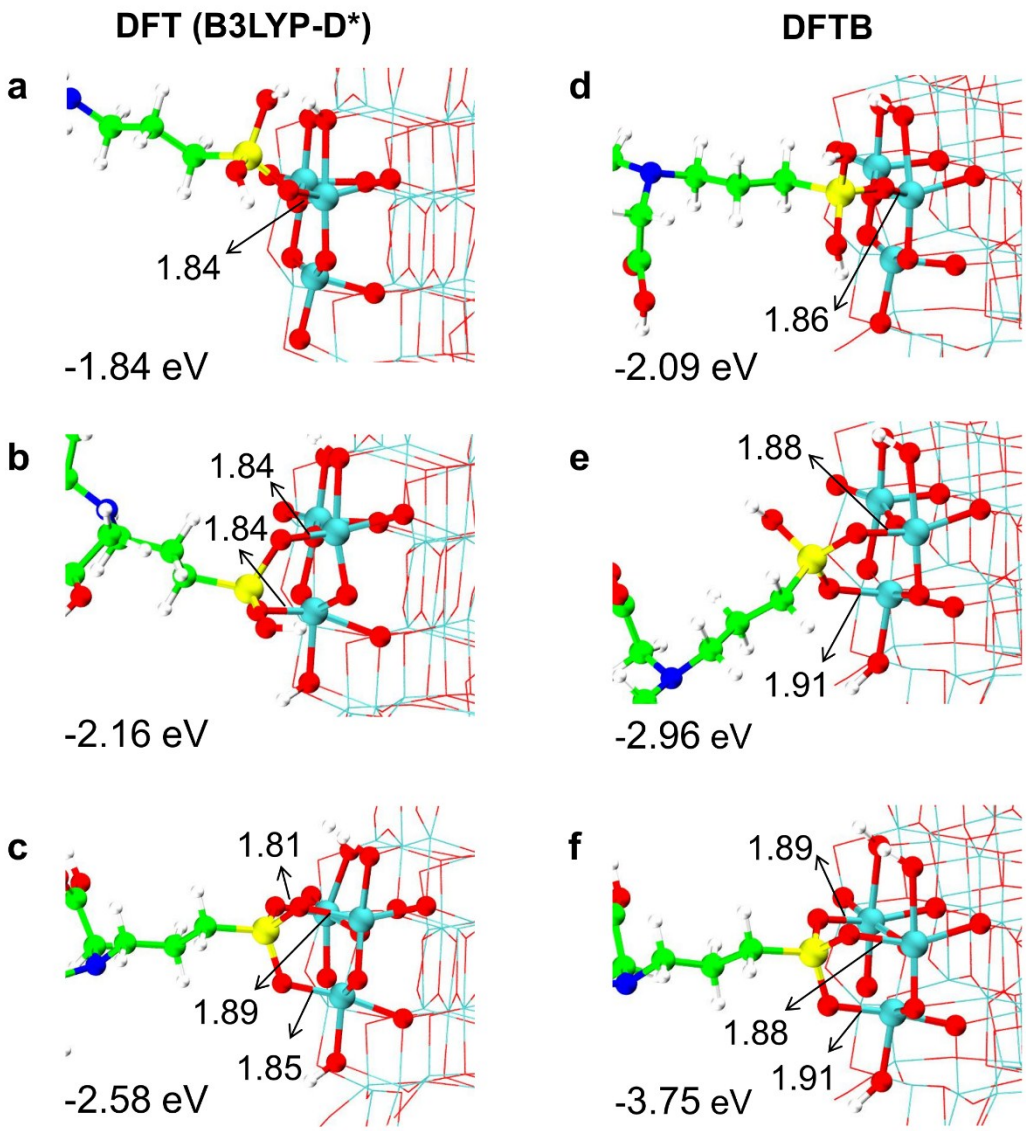


**Figure S1** Monodentate (a), bidentate (b), and tridentate (c) adsorption modes (side views) and adsorption energy per one TETT molecule (in eV) on the tri-site C of the spherical NP (Figure 2) as obtained by the DFT(B3LYP-D*) and DFTB. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atoms in yellow, C atoms in green, and N atoms in blue. Relevant covalent bonds are reported in Å in proximity of the bond.

**Table S1** Comparison between the mono-, bi- and tri-dentate adsorption mode (ΔE, in eV) for the TETT molecule on the $TiO_2$ nanoparticle with the DFT(B3LYP-D*) and the DFTB method for the tri-site C (Figure 2). The scaled DFTB values are also reported. The energy gain per bond is reported in parenthesis for each adsorption mode taken in account.

| | ΔE (eV) | | |
|---|---|---|---|
| | DFT(B3LYP-D*) | DFTB | scaled DFTB |
| | per ligand (per bond) | per ligand (per bond) | per ligand (per bond) |
| mono- | -1.84 (-1.84) | -2.09 (-2.09) | -1.84 (-1.84) |
| bi- | -2.16 (-1.08) | -2.96 (-1.48) | -2.16 (-1.08) |
| tri- | -2.58 (-0.86) | -3.75 (-1.25) | -2.58 (-0.86) |

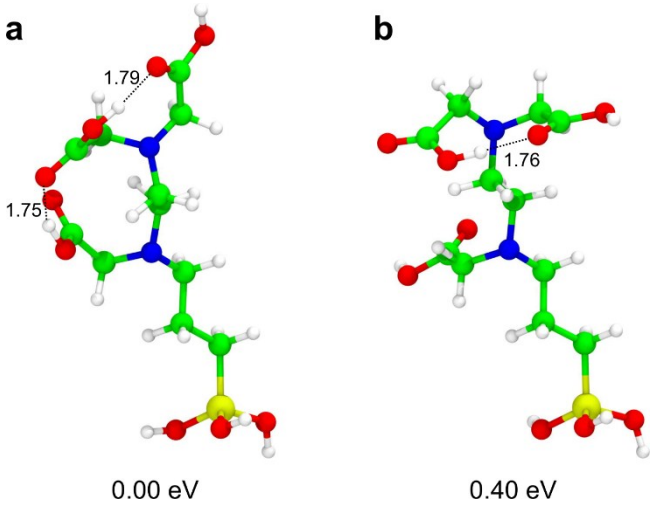


**Figure S2** Optimized last snapshot of the free TETT molecule from two different production runs. Si atoms in yellow, O atoms in red, H atoms in white, C atoms in green, and N atoms in blue. Relative energies values (in eV), with respect to the most stable **a** configuration, are reported below each structure. Intramolecular hydrogen bonds (in Å) are indicated with a dashed lines.

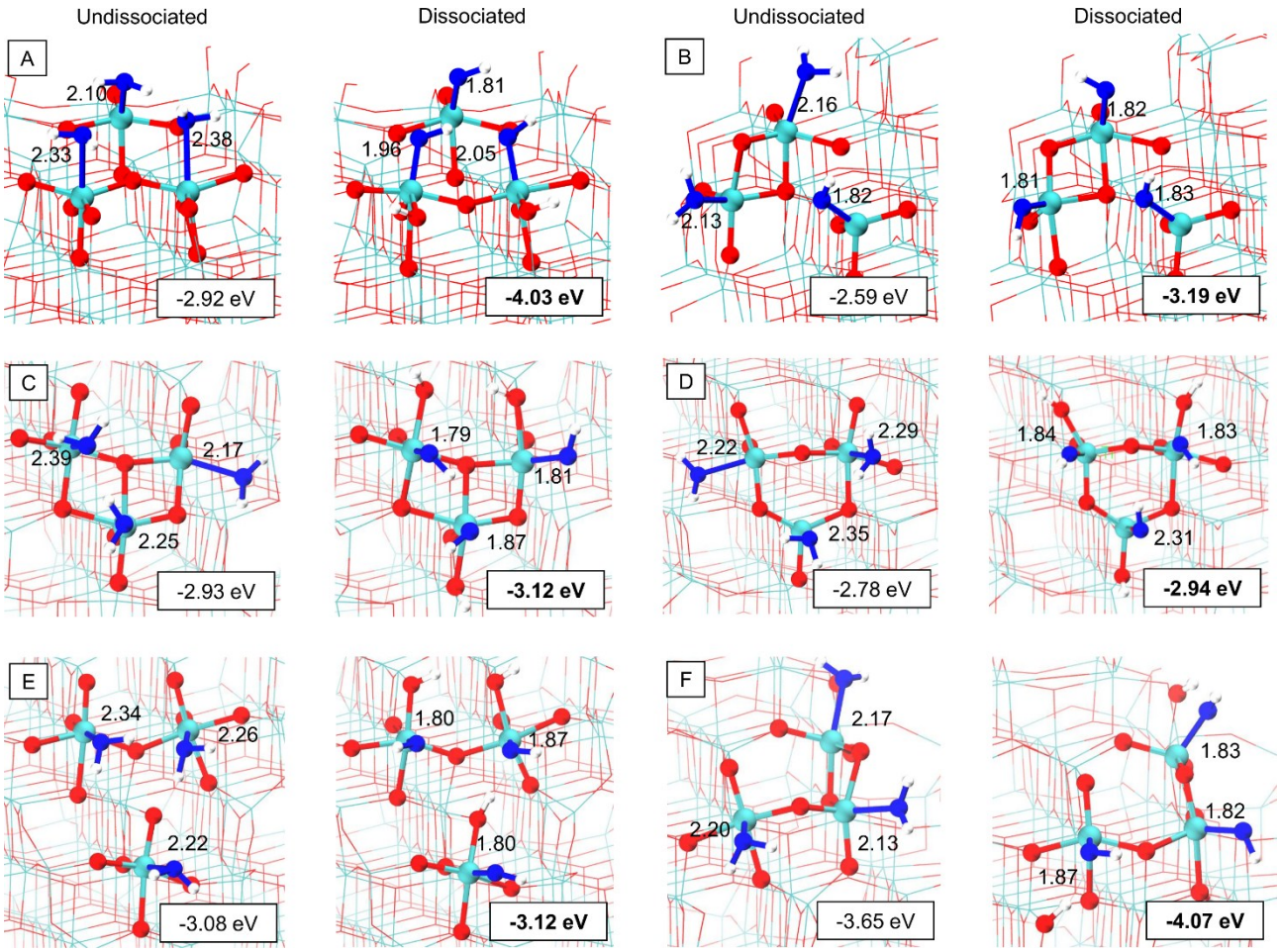


**Figure S3** Ball-and-stick representations of three undissociated and three dissociate water molecules on the identified tri-sites in Figure 2. Ti atoms are shown in cyan, H atoms in white, O atoms in red, and water O atoms in blue. Relevant bond lengths (in Å) and DFT (B3LYP-D*) adsorption energies (in eV) are also given below each structure.

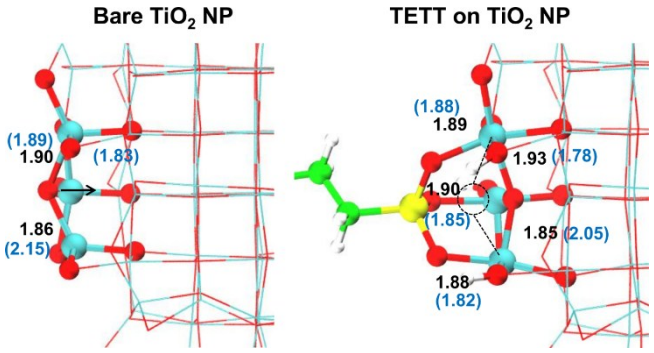


**Figure S4** On the right, top view of the tri-site C on the bare spherical NP, and on the left one TETT molecule adsorbed on the tri-site C (Figure 2), as obtained by DFTB-D3 and DFT (B3LYP-D*) calculations. The displacement of the $O_{2c}$ oxygen in the NP is show by dash lines due the TETT adsorption. Ti atoms are shown in cyan, O atoms in red, H atoms are shown in white, Si atom in yellow, C atoms in green, and N atoms in blue. Relevant distances, for both methods, are reported in Å. The DFT(B3LYP-D*) distances are detailed in parenthesis.

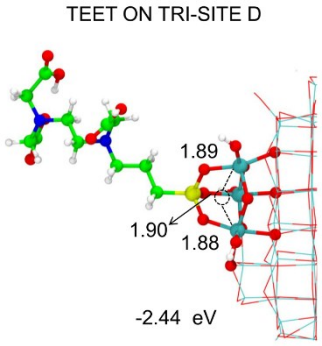


**Figure S5** Adsorption mode (side views) and adsorption energy per one TETT molecule (in eV) on tri site D (see Table 1) of the spherical NP as obtained by the DFTB-D3. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atoms in yellow, C atoms in green, and N atoms in blue. The displacement of the $O_{2c}$ oxygen in the NP is show by dash lines due the TETT adsorption. Relevant covalent bonds are reported in Å in proximity of the bond.

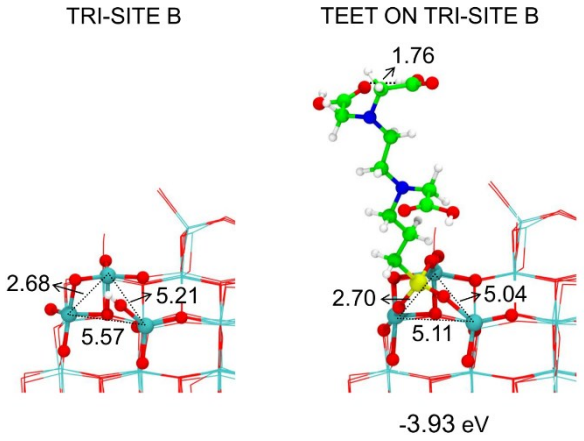


**Figure S6** On the right, side view of the tri-site B on the bare spherical NP and on the left one TETT molecule adsorbed on the tri-site B (see Table 1), as obtained by DFTB-D3. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atom in yellow, C atoms in green, and N atoms in blue. The Ti-Ti distances are show by dash lines in Å. The adsorption energy per one TETT molecule is in eV.

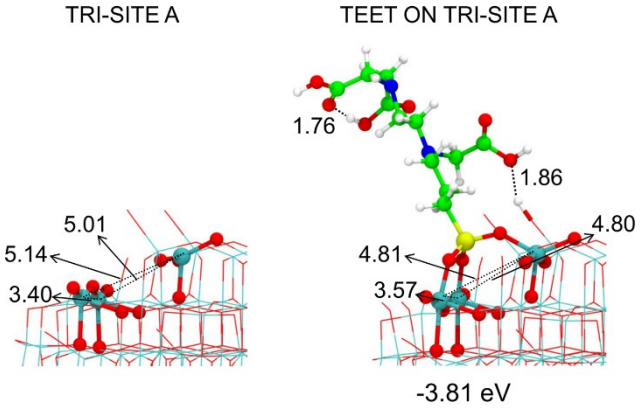


**Figure S7** On the right, side view of the tri-site A on the bare spherical NP and on the left one TETT molecule adsorbed on the tri-site A (see Table 1), as obtained by DFTB-D3. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atom in yellow, C atoms in green, and N atoms in blue. The Ti-Ti distances are show by dash lines in Å. Other relevant bonds are reported in proximity of the bond. The adsorption energy per one TETT molecule is in eV.

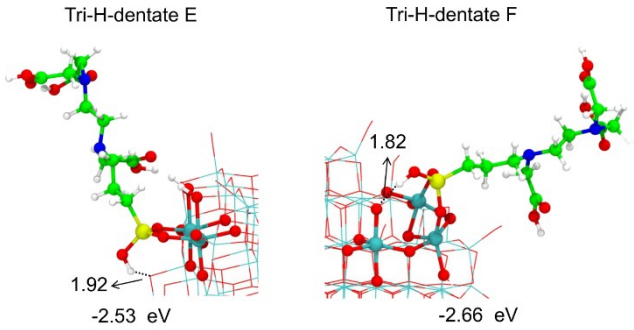


**Figure S8** Adsorption modes (side views) and adsorption energy per one TETT molecule (in eV) on the tri-H-bidentate E and tri-H-bidentate F sites (Table 1) of the spherical NP as obtained by the DFTB-D3. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atoms in yellow, C atoms in green, and N atoms in blue. H-bonds (in Å) are indicated with a dashed lines.

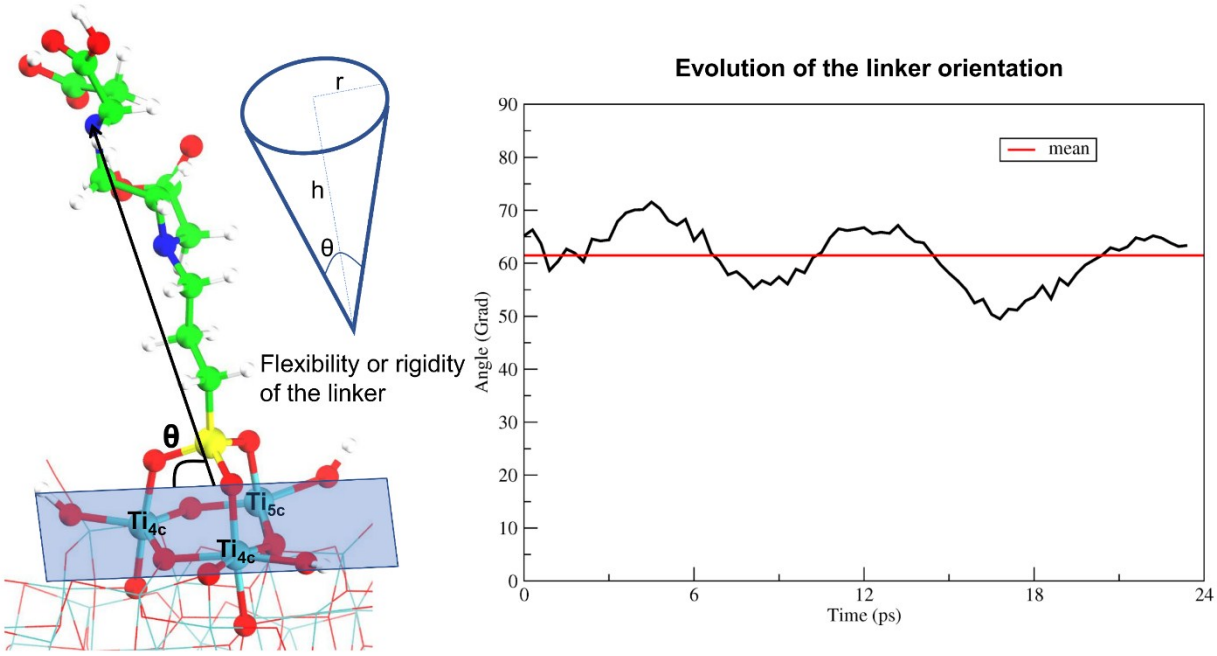


**Figure S9** On the left, the angle θ between the plane (in light blu), which contains the Ti atoms of the tri-site, and the vector (black arrow) that join the Si atom and the farthest N atom in the TETT molecule. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atom in yellow, C atoms in green, and N atoms in blue. On the right, the evolution of the angle θ for the tri-site D (Figure 2).

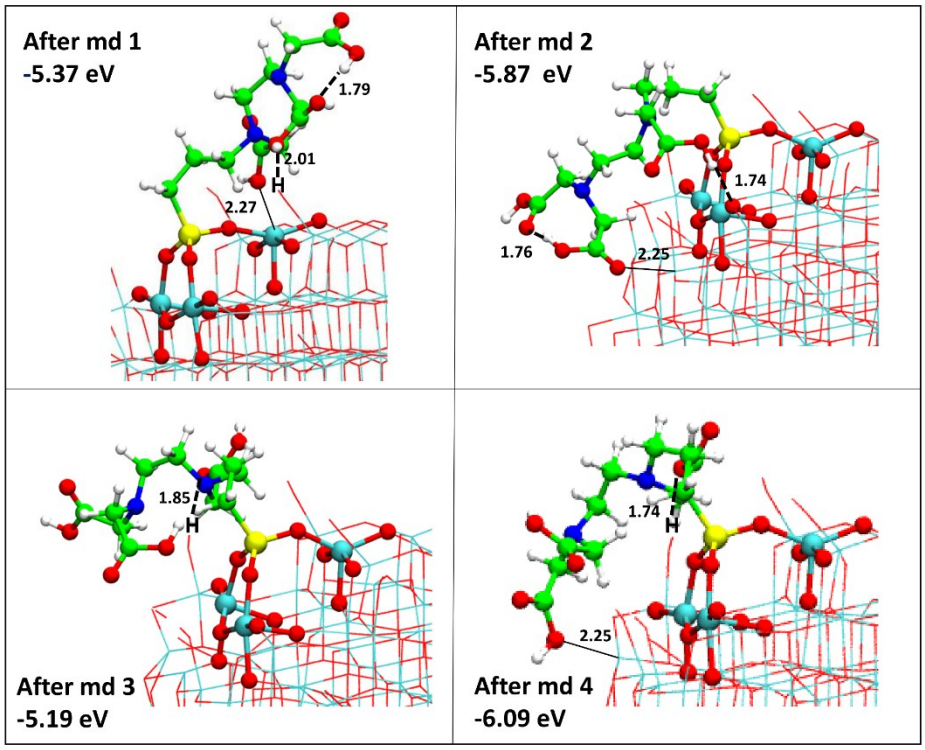


**Figure S10** Adsorption configurations (side views) and energies (in eV) for one TETT molecule on the tri-site A of the spherical NP (Figure 2) as obtained by DFTB-D3 calculations. The most stable configuration named After md 4 correspond to Figure 4b. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atoms in yellow, C atoms in green, and N atoms in blue. Relevant hydrogen bonds and coordinative bonds are represented by dashed lines and solid lines, respectively. Distances are reported in Å.

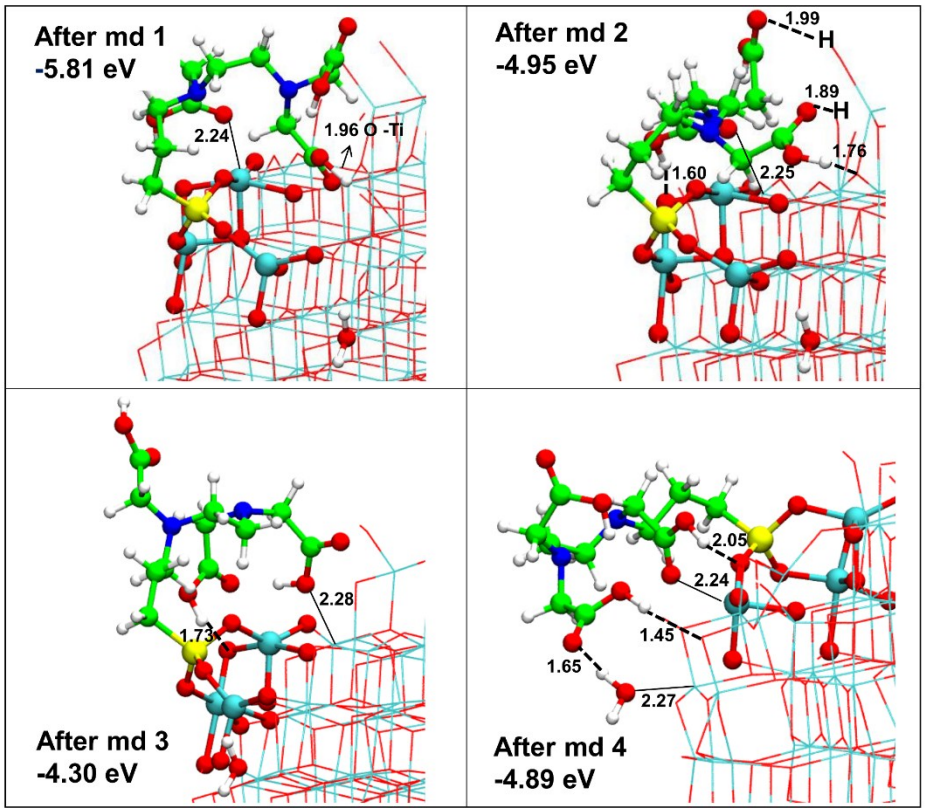


**Figure S11** Adsorption configurations (side views) and energies (in eV) for one TETT molecule on the tri-site B of the spherical NP (Figure 2) as obtained by DFTB-D3 calculations. The most stable configuration named After md 1 correspond to Figure 6b. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atoms in yellow, C atoms in green, and N atoms in blue. Relevant hydrogen bonds and coordinative bonds are represented by dashed lines and solid lines, respectively. Distances are reported in Å.

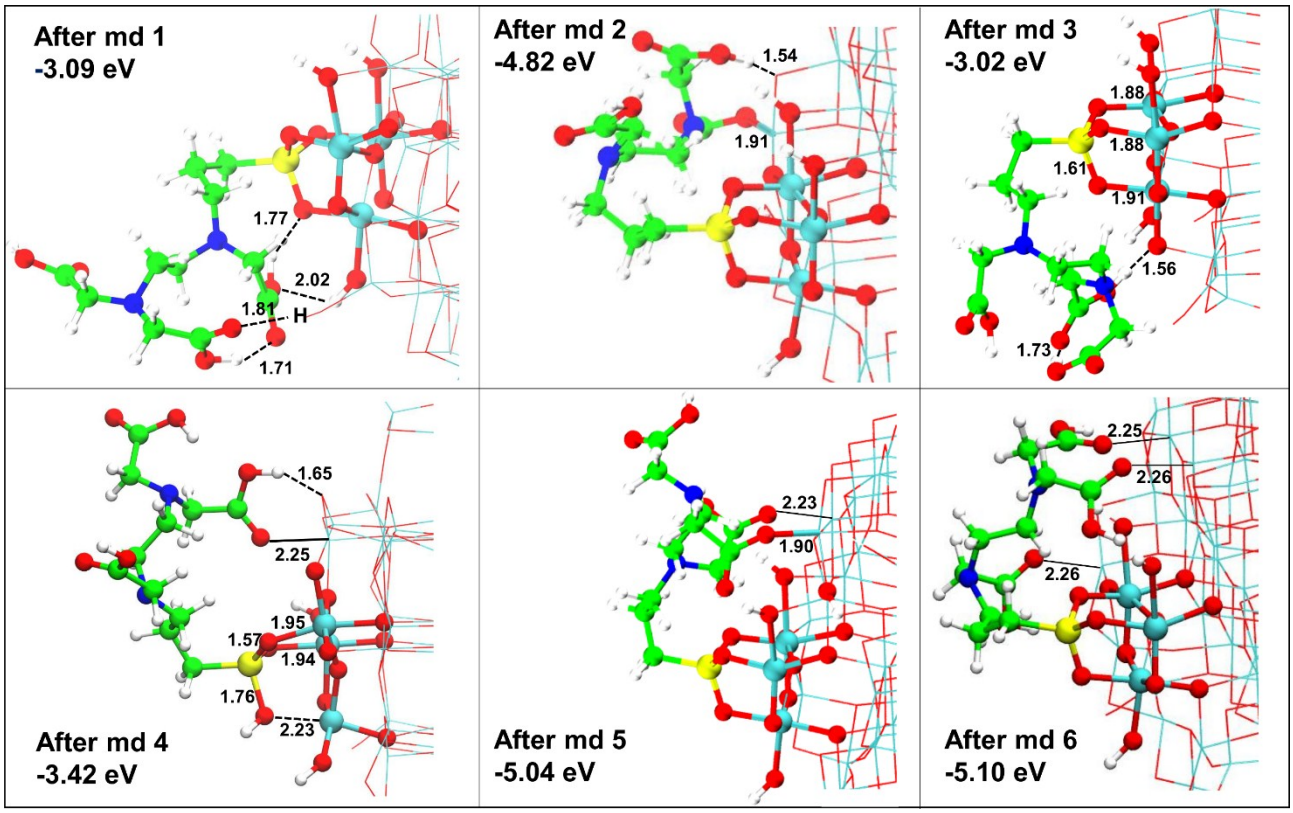


**Figure S12** Adsorption configurations (side views) and energies (in eV) for one TETT molecule on the tri-site C of the spherical NP (Figure 2) as obtained by DFTB-D3 calculations. The most stable configuration named After md 6 correspond to Figure 7b. Ti atoms are shown in cyan, O atoms in red, H atoms in white, Si atoms in yellow, C atoms in green, and N atoms in blue. Relevant hydrogen bonds and coordinative bonds are represented by dashed lines and solid lines, respectively. Distances are reported in Å.