Electronic Supplementary Material (ESI) for Energy & Environmental Science

Inherent Electronic Trap States in TiO_2 Nanocrystals: Effect of Saturation and Sintering

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Supporting Information

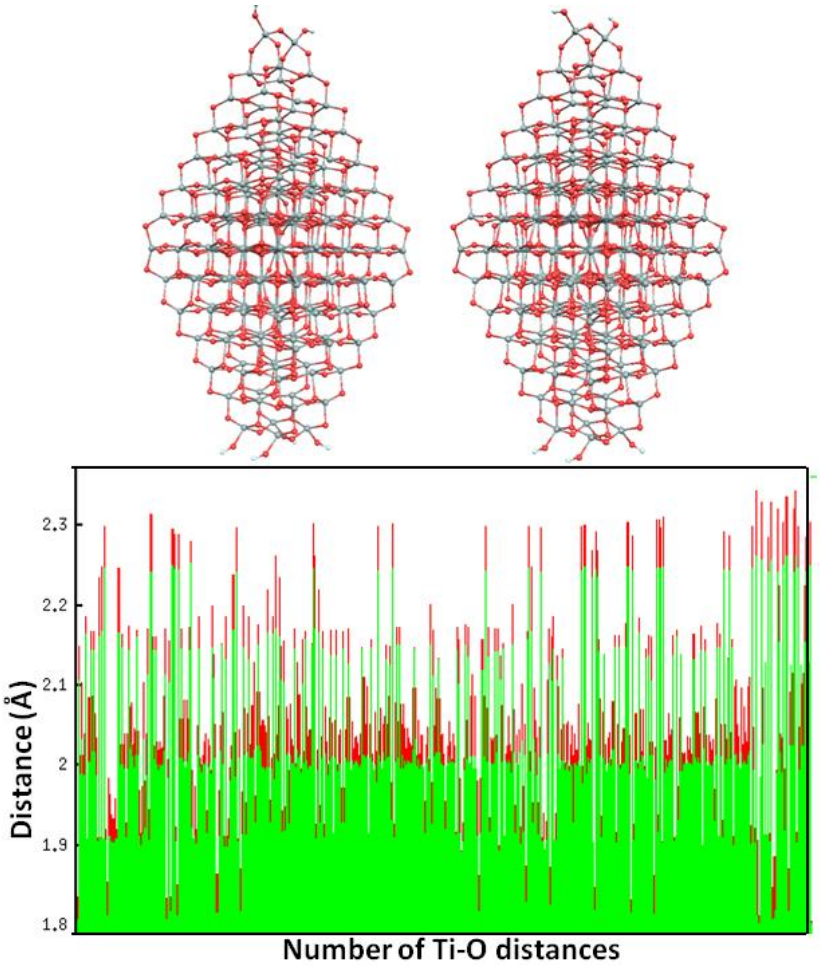

Figure S1. Upper panel: Optimized structure of the $(TiO_2)_{161}$-H_6 model by BP86/DZ (left) and DFTB (right). Lower panel: Differences in Angstrom between Ti-O distances for the $(TiO_2)_{161}$-H_6 model calculated by DFT (red) and DFTB (green). The DFTB distances are on average 1.35% shorter than the DFT ones.

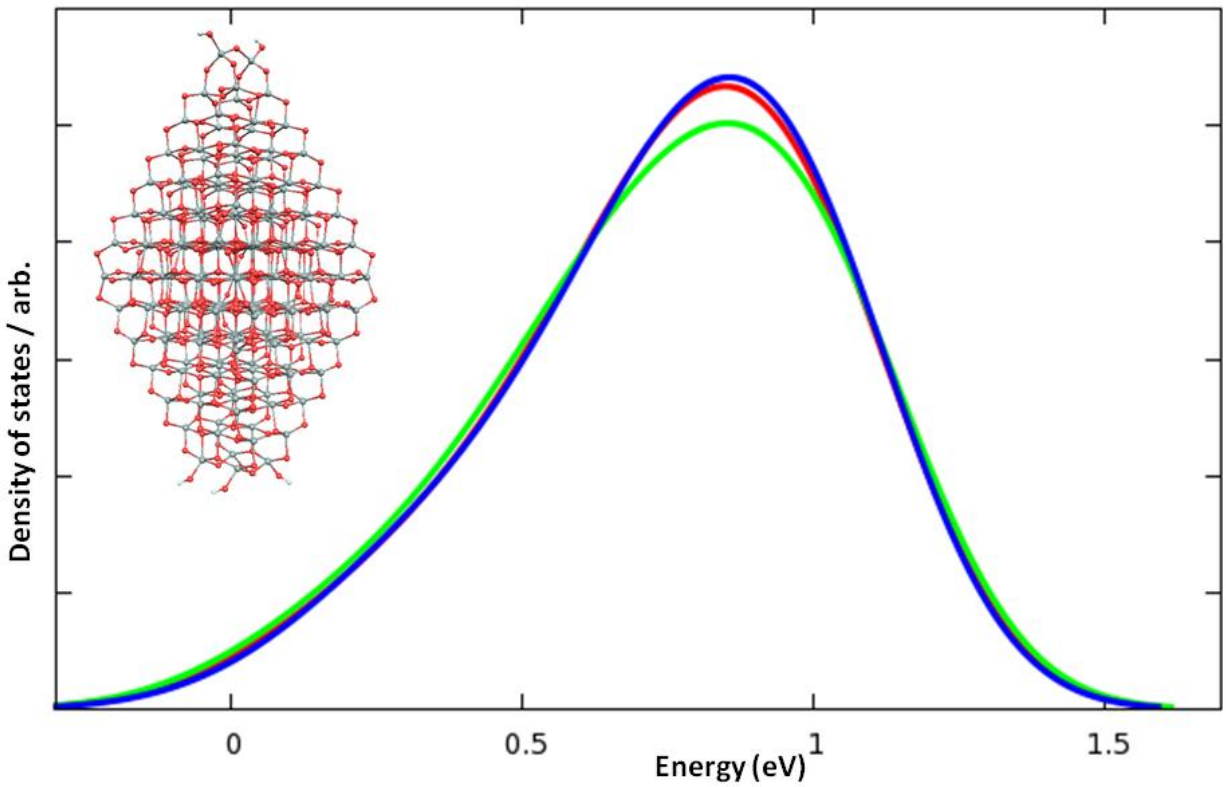

Figure S2. DOS profile (200 lowest unoccupied states) for the $(TiO_2)_{161}$-H_6 model, also shown as inset, calculated at the DFTB geometry by DFTB (red) and BP86/DZ (blue) levels of theory in vacuo and on the BP86/DZ geometry at the BP86/DZ level of theory (green line). The two DOS have been aligned at their maximum. The zero of the energy is set at the LUMO of the DFTB data set. (σ=0.18 eV)

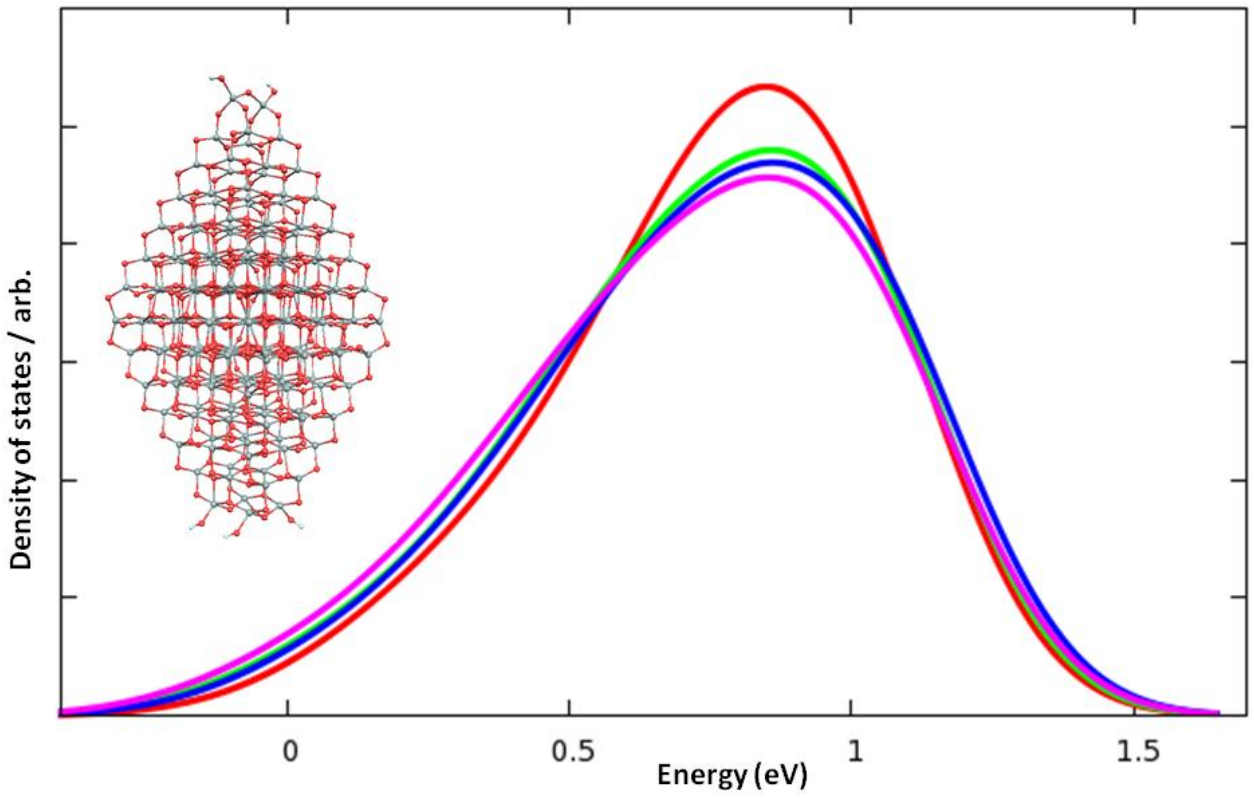

Figure S3. DOS profile (200 lowest unoccupied states) for the $(TiO_2)_{161}$-H_6 model, also shown as inset, calculated at the DFTB optimized geometry. DFTB (red), PBE/PW (green), BP86/DZ (blue line) and BP86/TZP (magenta line) levels of theory in vacuo. The three DOS have been aligned at their maximum. The zero of the energy is set at the LUMO of the DFTB data set. (σ=0.18 eV)

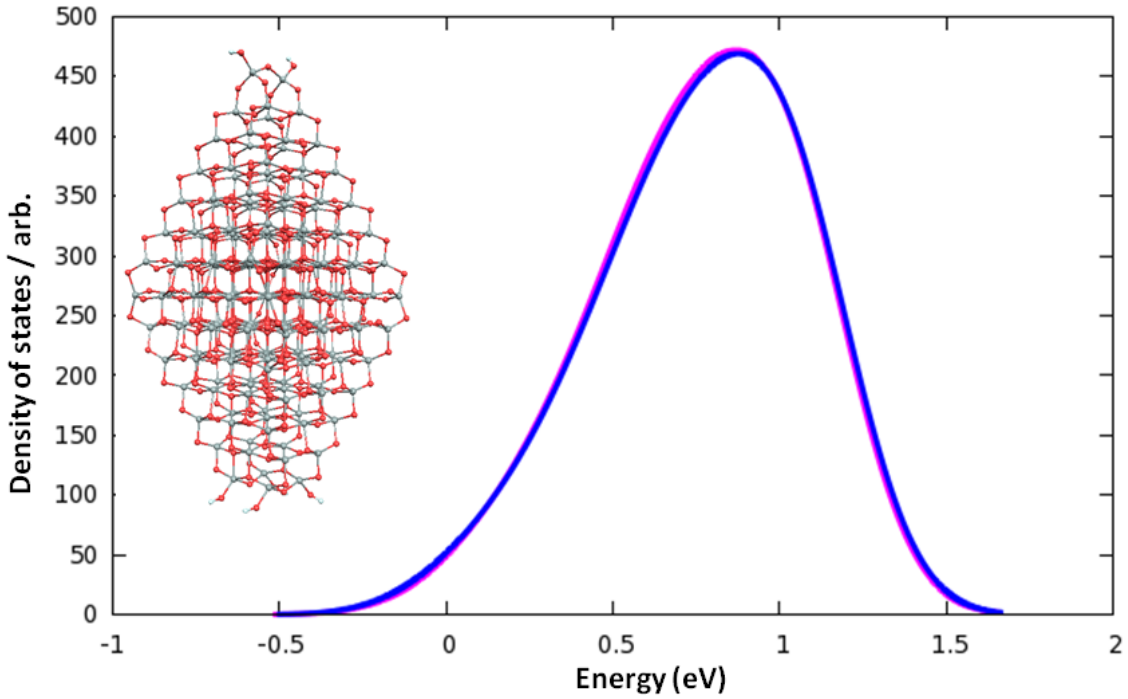

Figure S4. DOS profile (200 lowest unoccupied states) for the $(TiO_2)_{161}$-H_6 reduced model, also shown as inset, calculated at the DFTB optimized geometry. BP86/DZ level of theory in vacuo (blue) and in water solution (magenta), simulated by a dielectric continuum. The two DOS have been aligned at their maximum. The zero of the energy is set at the LUMO of the vacuo data set. (σ=0.18 eV)

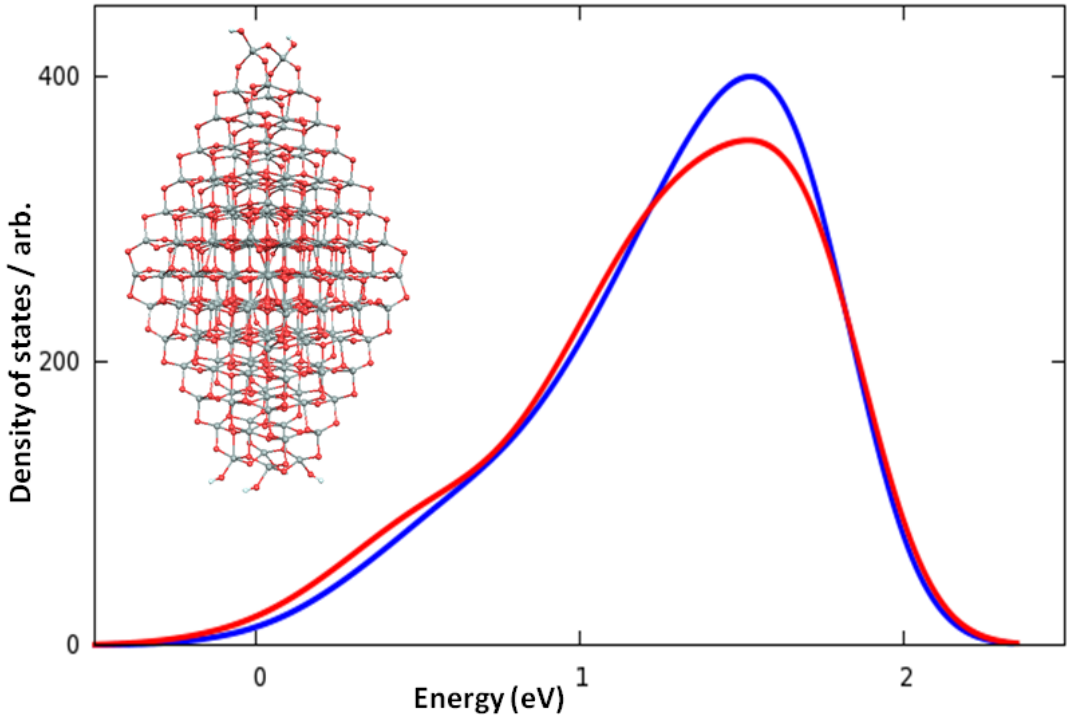

Figure S5. DOS profile (200 lowest unoccupied states) for the $(TiO_2)_{161}$-H_6 reduced model, also shown as inset, calculated at the DFTB optimized geometry. BP86/SZ (blue line) and B3LYP (red line) in solvent. The two DOS have been aligned at their maximum. The zero of the energy is set at the LUMO of the BP86 data set. (σ=0.18 eV)

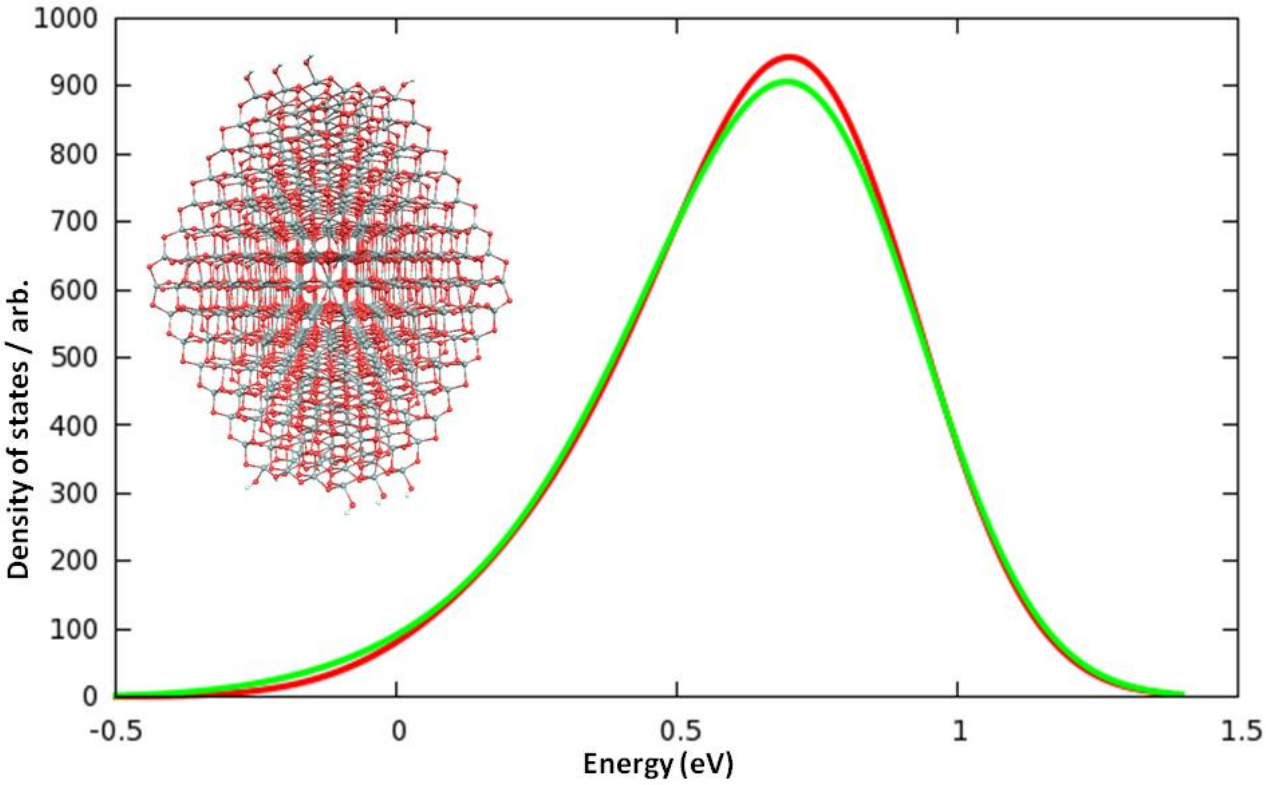

Figure S6. DOS profile (300 lowest unoccupied states) for the $(TiO_2)_{411}$-H_{16} model **1**, also shown as inset, calculated at the DFTB optimized geometry. DFTB (red) and PBE/PW (green levels of theory in vacuo. The two DOS have been aligned at their maximum. The zero of the energy is set at the LUMO of the DFTB data set. (σ=0.18 eV)

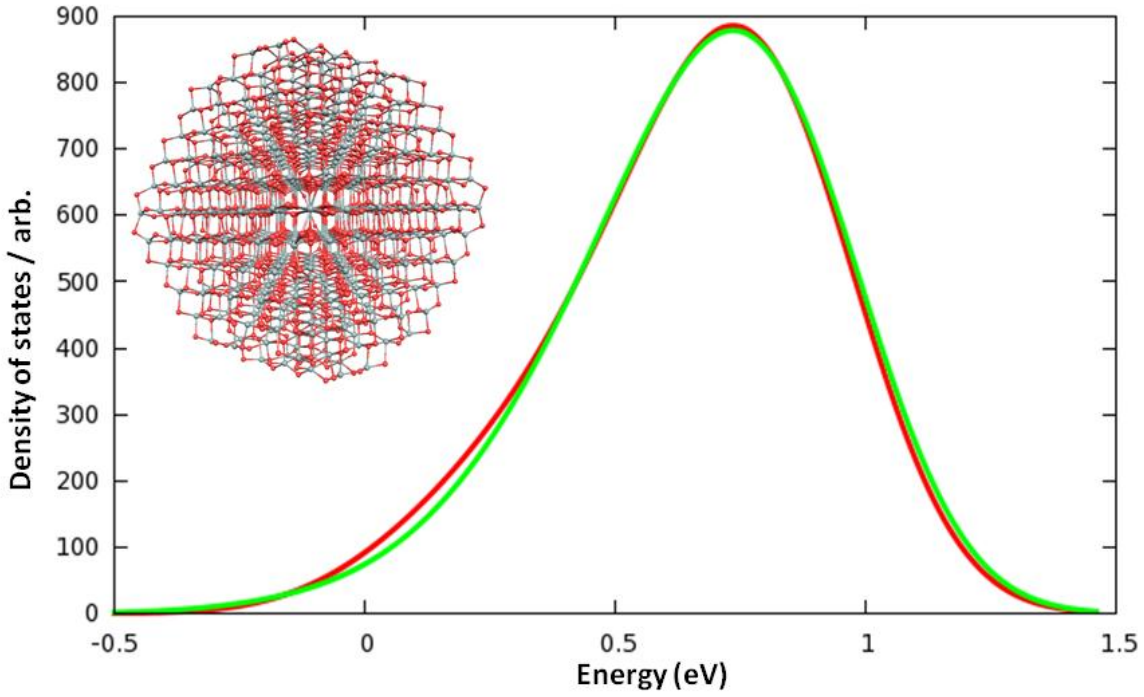

Figure S7. DOS profile (300 lowest unoccupied states) for the $(TiO_2)_{367}$ model **2**, also shown as inset, calculated at the DFTB optimized geometry. DFTB (red) and PBE/PW (green) levels of theory in vacuo. The two DOS have been aligned at their maximum. The zero of the energy is set at the LUMO of the DFTB data set. (σ=0.18 eV)

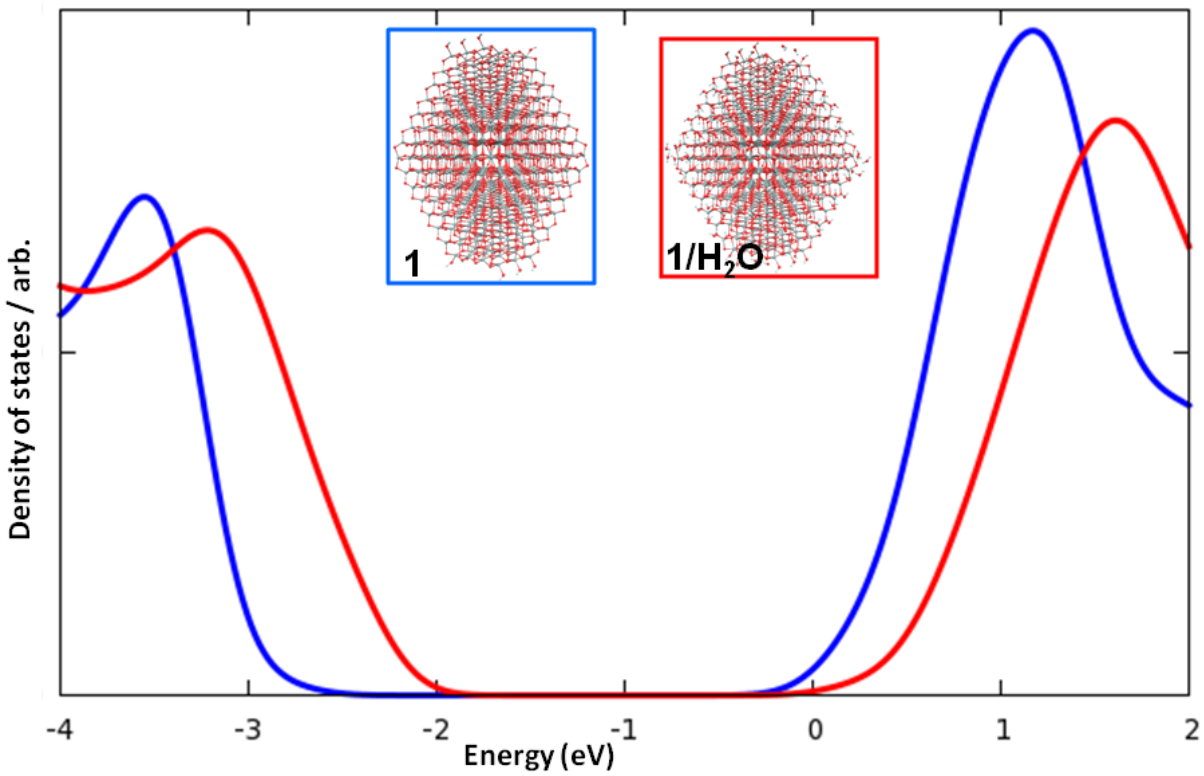

Figure S8. DOS profile (300 lowest unoccupied states) for the models **1** (blue) and **1/H_2O** (red) calculated at the DFTB level of theory (σ=0.08 eV). The zero of the energy is set at the LUMO of **1**.

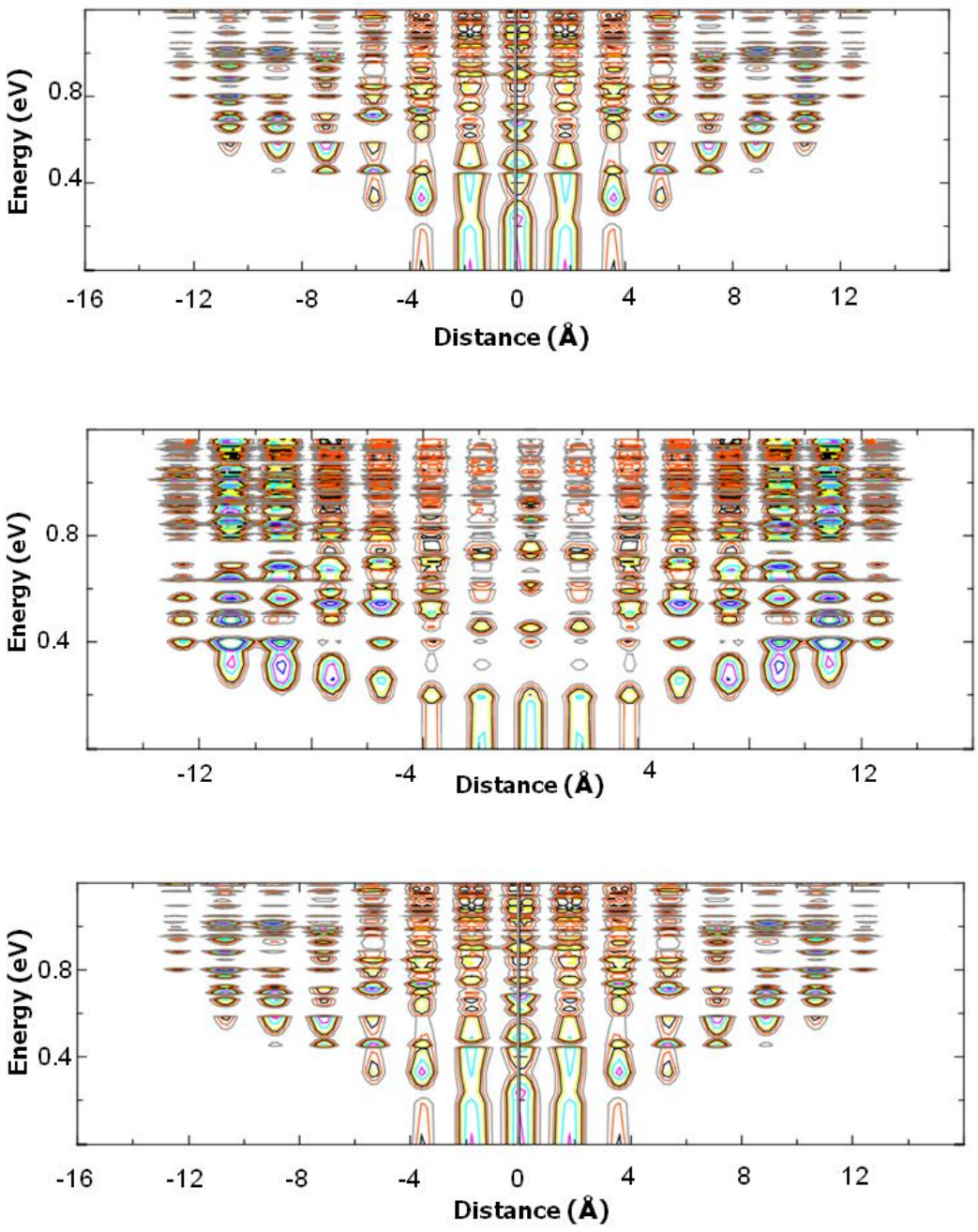

Figure S9. Top: Contour plot of the space/energy (eV) diagram for the DOS of unoccupied states of NC **2**, scanned along the length of the NC. Middle: Contour plot of the space/energy (eV) diagram for the DOS of unoccupied states of NC **1**, scanned along the length of the NC. Bottom: Contour plot of the space/energy (eV) diagram for the DOS of unoccupied states of NC **1/154H_2O**, scanned along the length of the NC.

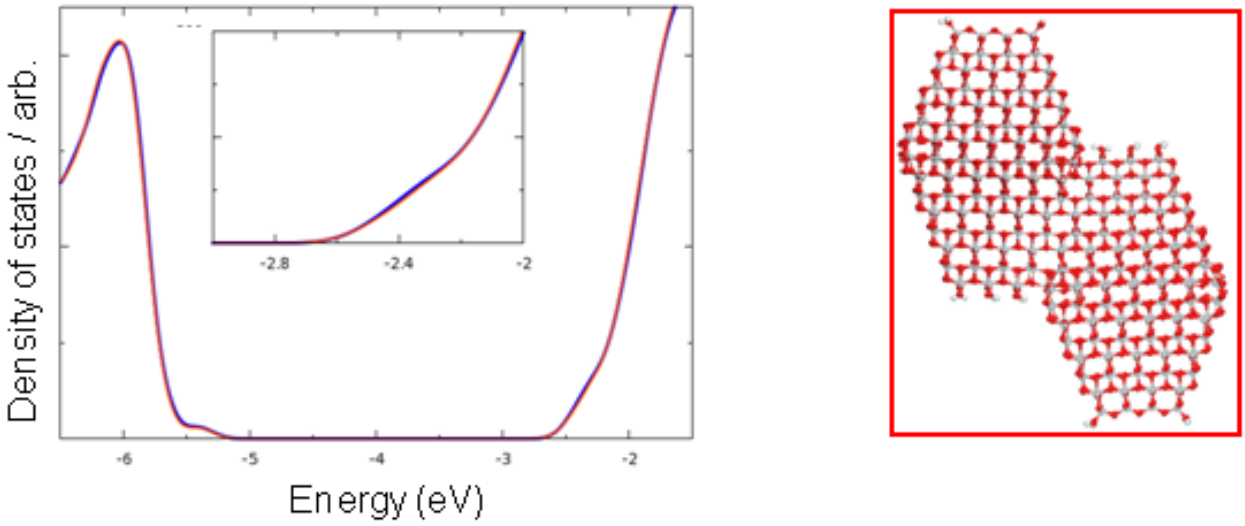

Figure S10. Optimized geometry for two interacting NCs (model **1**) via the 101/101 surfaces along with the corresponding DOS (red curve) compared to that of the isolated model **1** (blu curve) calculated at the DFTB level of theory (σ=0.18 eV).