Supporting Information: Dopamine-decorated TiO_2 nanoparticles in water: a QM/MM vs an MM description

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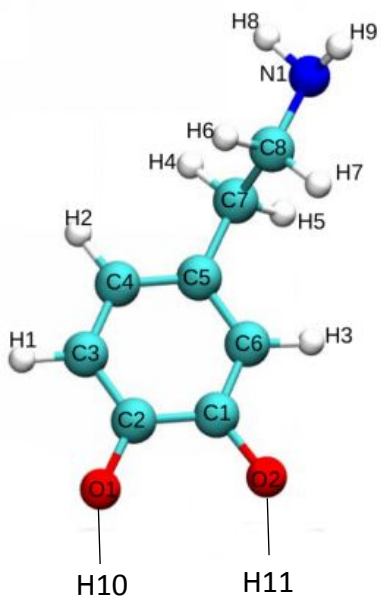
Table S1. Partial atomic charges on the atoms of a dissociated dopamine on the NP from HF, DFT, and SCC-DFTB calculations. (Atomic charge is in unit e).

Atom-type	HF†	DFT‡	DFTB‡
O1	-0.56010	-0.65105	-0.36635
O2	-0.55408	-0.64807	-0.39316
C1	0.33646	0.13254	0.21764
C2	0.32326	0.13956	0.20965
C3	-0.37992	-0.18323	-0.19040
C4	-0.15126	-0.13775	-0.14715
C5	-0.00648	-0.21999	0.00822
C6	-0.43803	-0.09793	-0.22691
H1	0.17834	0.20243	0.08405
H2	0.14569	0.18076	0.07888
H3	0.19300	0.19984	0.08882
C7	-0.03289	-0.30852	-0.13215
H4	0.04809	0.16501	0.06637
H5	0.04809	0.17049	0.06938
C8	0.40929	-0.04451	0.01760
H6	-0.03388	0.14601	0.04013
H7	-0.03388	0.13469	0.03778
N1	-1.04833	-0.65865	-0.46571
H8	0.36938	0.22590	0.19267
H9	0.36938	0.22843	0.19226
H10	0.41012	0.49056*	0.33423*
H11	0.40777	0.48158*	0.33373*



† single-dopamine molecule in vacuum

‡ partial atomic charges averaged over all dopamine molecules on the nanoparticle.

* undissociated hydrogen atoms bonded to the O1 and O2 atoms, respectively.

Table S2. Comparison of binding energy (in eV) of a single molecular water at three Ti sites on the bare anatase TiO_2 NP surface calculated at the DFT, DFTB, QM(DFTB)/MM and MM level of theory with the original Matsui-Akaogi (MA) or reparametrized Matsui-Akaogi (OPT) force fields. For the Ti sites numbering and for DFT and DFTB data see Ref.: Fazio, G. et al. *ACS Appl. Mater. Interfaces* **2018**, *10*, 29943−29953.

Method/Ti site	**Ti_{5c}(4)**	**Ti_{5c}(5)**	**Ti_{5c}(14)**
DFT	-0.92	-0.55	-1.57
DFTB	-1.00	-0.41	-1.17
QM(DFTB)/MA	-0.61	-0.49	-0.66
QM(DFTB)/OPT	-0.36	-0.43	-0.40
MA	-1.10	-1.33	-1.21
OPT	-1.64	-1.27	-1.27

Table S3. Comparison of Ti-O_w distance (in Å) of a single molecular water at three Ti sites on the bare anatase TiO_2 NP surface calculated at the DFT, DFTB, QM(DFTB)/MM and MM level of theory with the original Matsui-Akaogi (MA) or reparametrized Matsui-Akaogi (OPT) force fields. For the Ti sites numbering and for DFT and DFTB data see Ref.: Fazio, G. et al. *ACS Appl. Mater. Interfaces* **2018**, *10*, 29943−29953.

Method/Ti site	**Ti_{5c}(4)**	**Ti_{5c}(5)**	**Ti_{5c}(14)**
DFT	2.22	2.30	2.10
DFTB	2.28	2.29	2.27
QM(DFTB)/MA	2.52	*3.10***	2.56*
QM(DFTB)/OPT	*3.73**	*3.77***	*3.74**
MA	2.36	2.50*	2.46*
OPT	*5.99***	*3.70***	*3.75**

Numbers in italic indicate that there is no Ti—O_w bond but only H-bond intraction.

*single H-bond with the exposed Oxygen atoms nearby the Ti site.

**two H-bonds with the exposed Oxygen atoms nearby the Ti site.

Table S4. Comparison of tilt angle (θ, degrees) between surface-bonded dopamine ligands with the NP surface in vacuum (T=300K). Experimental Carbon K-edge X-ray absorption fine structure (NEXAFS) and high-level DFTB predictions are compared with *in silico* low-level MM-MD predictions with the original Matsui-Akaogi (MA) or reparametrized Matsui-Akaogi (OPT) force fields with the HF point-charge model. Percentage of dopamine ligands for each state are shown in parenthesis. Open-state corresponds to dopamine ligands with θ < 20°. Intermediate means dopamine ligands within the range of 20°< θ < 45°. Closed-state refers to dopamine ligands with θ > 45°. Experimental tilt angle value from Ref.: Syres, K. et al. *Langmuir* **2010**, *26*, 14548–14555.

Method/<tilt angle>	**open-state**	**intermediate**	**closed-state**	**overall**
Experimental	5°	-	-	-
DFTB	12° (46%)	32° (27%)	56° (27%)	29
b-OPT	12° (55%)	31° (40%)	45° (5%)	21
MA	11° (7%)	37° (20%)	68° (73%)	58

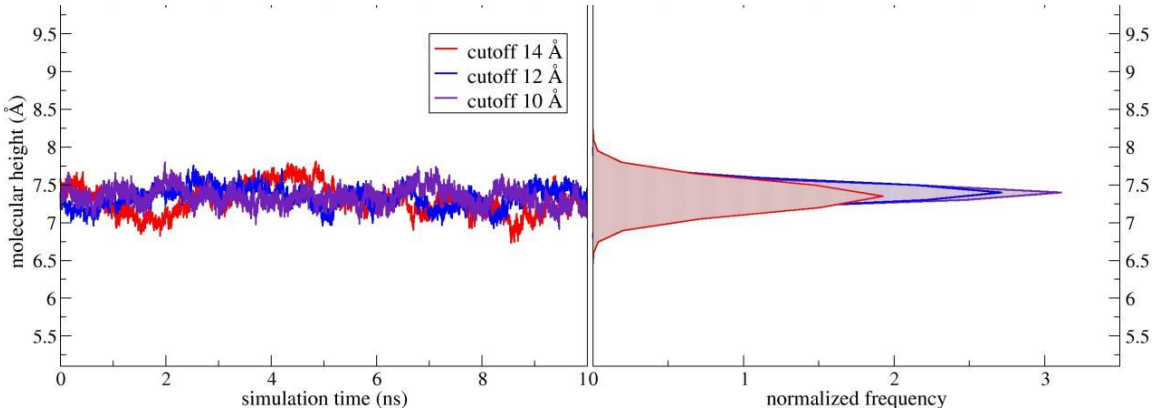


Figure S1. Effect of increasing nonbonded cutoff on the molecular height of bonded-dopamine on the NP surface. Three different nonbonded cutoffs were tested (10 Å, 12 Å, and 14 Å) in the MM-MD simulations. Increasing of the non-bonded cutoff broader the distribution of molecular height of dopamine for larger values, although no significant changes has been found on their average values.

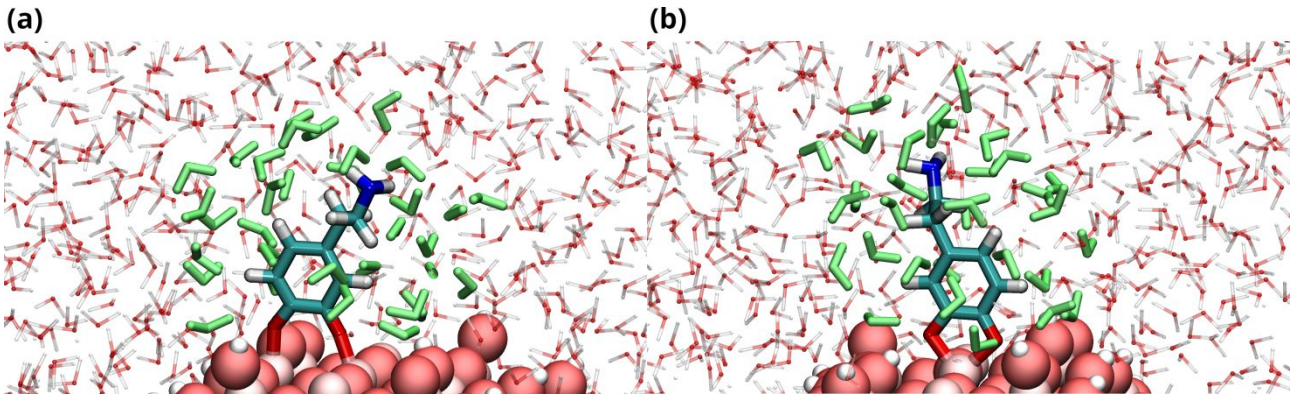


Figure S2. Final MD snapshots of molecular structures for a) bidentate and b) chelated binding modes of dopamine anchored to the TiO_2-NP and immersed in bulk water. Atom colors are: Oxygen (red), Carbon (cyan), Hydrogen (white), and Titanium (pink). Solvating water molecules within a radius of 5 Å around the dopamine ligand are highligthed in green.

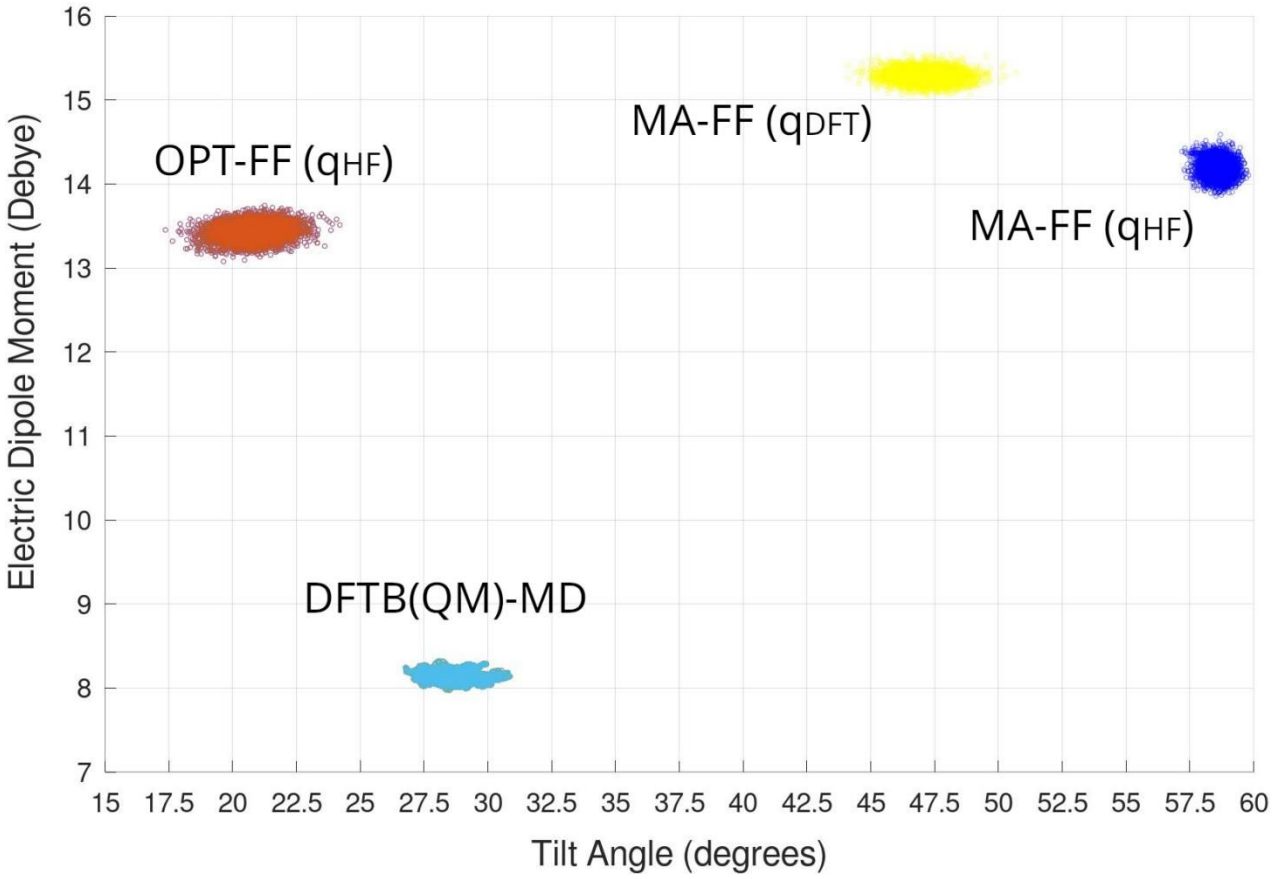


Figure S3. Average tilt angle versus dipole moment of dopamine ligands on the anatase TiO_2 NP surface estimated at QM(DFTB) and MM levels of theory in vacuum. At MM level, we tested OPT and MA force fields. Color coding: cyan (DFTB), brown (OPT, q_{HF}), yellow (MA, q_{DFT}) and blue (MA, q_{HF}).