

## Supporting Information

### First-principles study of ruthenium(II) sensitizer adsorption on anatase TiO<sub>2</sub> (001) surface anatase TiO<sub>2</sub> (001) surface

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### Detailed information for structure T1

Structure T1 may appear after the rotation of structure B1 along its rotation axis (O2-O5). The geometrical configuration of T1 and its partial enlarged view are shown in Fig. S1. It is clearly seen that, for the newly formed attachment of the third carboxylic group, the H atom remains in the carboxylic group and the distances of H atom with its two nearest O<sub>2c</sub> atoms are 2.69 Å and 2.53 Å, respectively. Moreover, the length of Ti<sub>5c</sub>-O bond is 2.15 Å, larger than the bond lengths of Ti<sub>5c</sub>-O2 and Ti<sub>5c</sub>-O5 (1.90 Å and 2.01 Å, respectively), indicating that the bonding between the third carboxylic group and TiO<sub>2</sub> surface is weaker than those of other two attached carboxylic groups. Whereas, in structures B2 and B3, both monodentate and bidentate modes of coordination are formed with dissociated H atoms transferred to the O<sub>2c</sub> atoms. It is thus that the adsorption energy of structure T1 is smaller than those of structures B2 and B3.

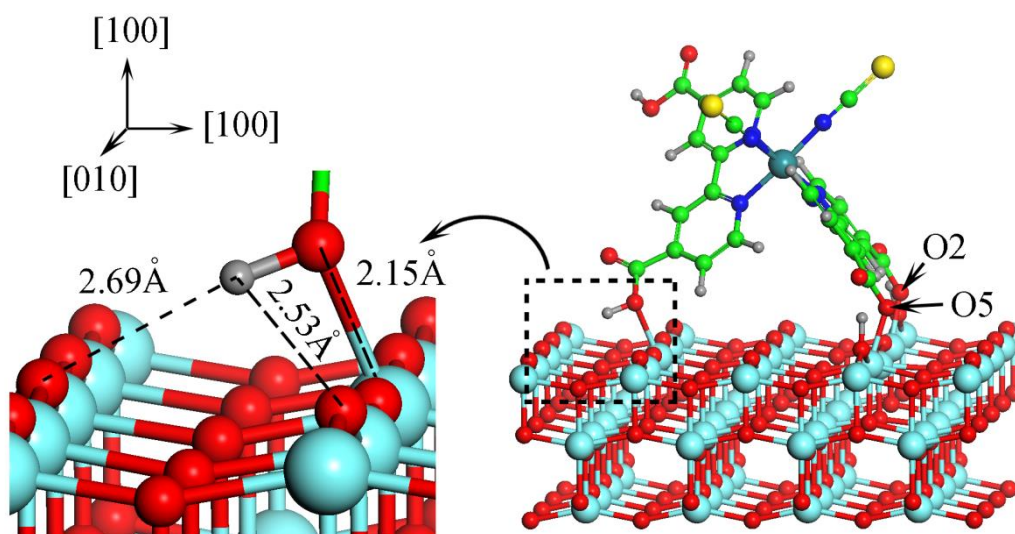


Fig. S1. Geometrical configuration of T1 along [010] direction and its partial enlarged view. Green, red, blue, yellow, gray, aquamarine and cyan spheres represent C, O, N, S, H, Ru and Ti atoms, respectively.

### **Influence of acetonitrile solvent for the stability of structure B5 and T2**

Acetonitrile is one of the most widely used solvent in dissolving the dye molecule while the sensitized semiconductor is fabricated. We have performed the calculation of the acetonitrile molecular adsorption on  $\text{TiO}_2$  (001) surface without N3 molecule. According to our calculation, the acetonitrile molecule is adsorbed on the (001) surface thru  $\text{Ti}_{5c}$ -N bonding with a bond length of 2.15 Å and an adsorption energy of 1.59 eV, suggesting a dense acetonitrile molecular layer can be formed on  $\text{TiO}_2$  (001) surface.

Except for the four bonded  $\text{Ti}_{5c}$  atoms, there are two  $\text{Ti}_{5c}$  atoms under the N3 molecule available for solvent adsorption in both structures B5 and T2 (see Fig. 2 and Fig. S2) . These two  $\text{Ti}_{5c}$  atoms have great influence on the adsorption of N3 molecule, in consideration of the steric effect between the acetonitrile and N3 molecules. To check the relative stability of structures B5 and T2 under the circumstance of solution, we have performed calculations of structures B5 and T2 with two additional acetonitrile molecules. As shown in Fig. S2, for structure B5, two acetonitrile molecules are sited on different sides of N3 molecule and are oriented in opposite directions. While for structure T2, due to the attachment of the third carboxylic group, two acetonitrile molecules have to orient in the same direction with increased total energy. Eventually, under the condition of adsorption of two acetonitrile molecules, the B5 structure is more stable than structure T2 by 0.22 eV. It is confirmed that structure B5 could be more preferable than structure T2 under the solution condition.

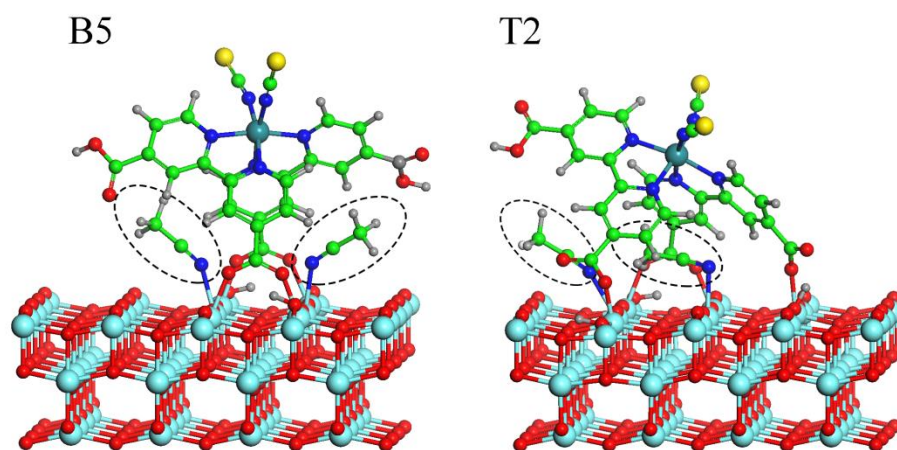


Fig. S2. Optimized geometrical structures of B5 and T2 with the adsorption of two acetonitrile molecules. The acetonitrile molecules are bonded with the surface  $\text{Ti}_{5c}$  atoms under the N3 molecules.

### **N3 molecule adsorbed on (101) surface**

The possible configurations of N3 molecular adsorption on anatase TiO<sub>2</sub> (101) surface are shown in Fig. S3. In structures F1, F2 and F3, the N3 molecules are anchored on the (101) surface initially with their fully protonated forms. Unlike the cases on (001) surface, after relaxation, all H atoms still remain in the carboxylic groups of N3 molecule, indicating that the O<sub>2c</sub> atoms of (101) surface are more inert than those of (001) surface. However, in actual DSSCs, under the solution conditions, the N3 molecule is easily to be partly deprotonated<sup>[1]</sup>. To mimic the experimental situation, we have initially transferred two H atoms of N3 molecule to the surface bridge O<sub>2c</sub> atoms and obtained the optimized geometrical structures D1~ D4 and E1, as shown in Fig. S3.

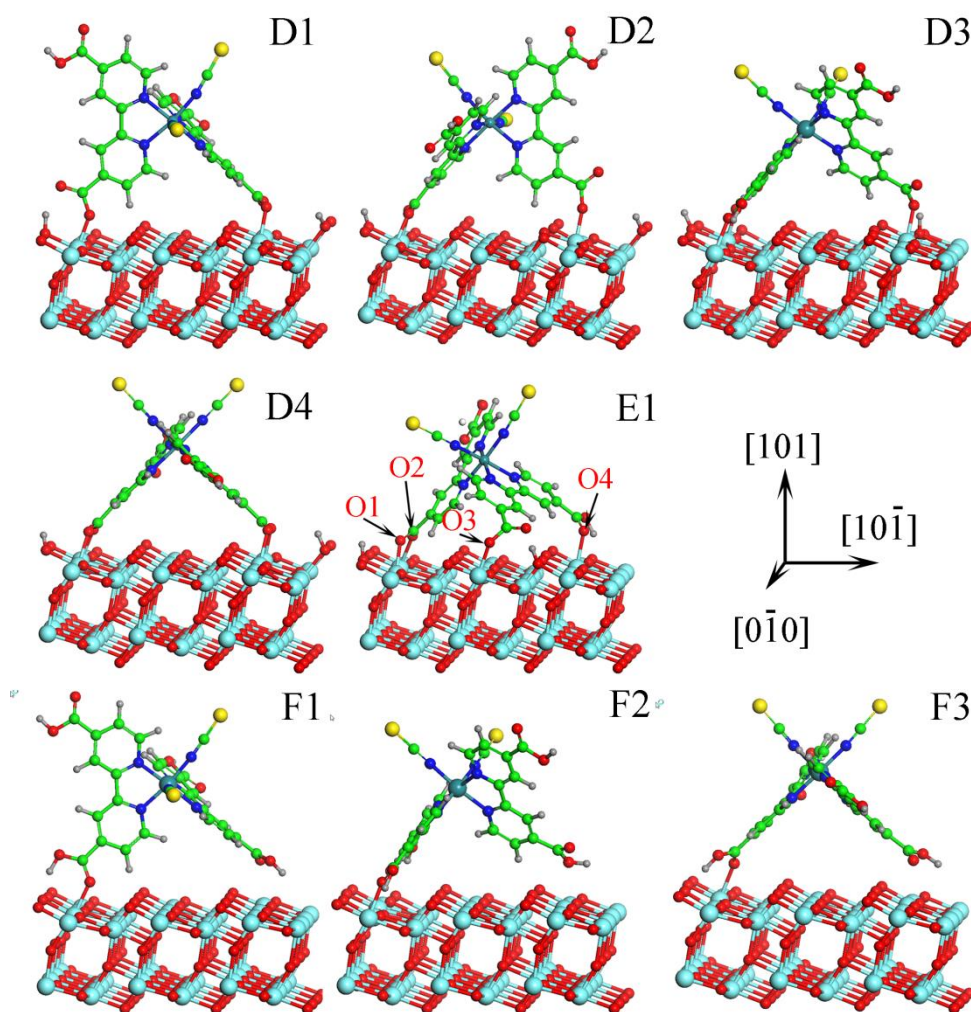


Fig. S3 Optimized geometrical structures of N3 molecule adsorbed on anatase (101) surface.

The adsorption energies of N3 molecule in each structure, calculated by using LDA and PBE0 methods, are listed in Table S1. The adsorption energy of N3 molecule in each structure using PBE0 functional is decreased by 1~1.5 eV, compared to the

results from LDA method. In both PBE0 and LDA methods, structure D4 and E1, similar with structure G and I<sub>2</sub> in Ref.2, respectively, are the two most energetically stable structures. While for the relative stability of structure D4 and E1, the total energy of structure E1 is 0.57 eV lower than that of structure D4 by using LDA method. It is also found that, in Ref.2, structure G is the most preferable configuration, with its energy 21.07 kcal/mol (0.91 eV) lower than that of structure I<sub>2</sub>. However, by using PBE0, structure D4 is more stable than structure E1 by 0.15 eV. Since the structural optimization is performed by using LDA method in our calculation, as the computation cost of PBE0 is too expensive, we believe that the different trend of adsorption energies between LDA and PBE0 is due to the structural optimization. By using LDA method, the most energetically preferable configuration is structure E1 with an adsorption energy of 3.84 eV, forming four Ti<sub>5c</sub>-O bonds between the N<sub>3</sub> molecule and TiO<sub>2</sub> surface. For ease of comparison, the lengths of Ti<sub>5c</sub>-O bonds of structure E1 in our work and those of similar structure in other work<sup>[2]</sup> are shown in Table S2. The values agree quite well.

Table S1. Calculated adsorption energies (eV) of N<sub>3</sub> molecule on TiO<sub>2</sub> (101) surface.

Structure	D1	D2	D3	D4	E1	F1	F2	F3
LDA	2.74	2.35	2.89	3.29	3.86	2.30	2.29	2.23
PBE0	1.26	1.03	0.57	1.70	1.55	1.12	0.75	0.83

Table S2. Comparison of Ti<sub>5c</sub>-O bond lengths (Å) between structure E1 and structure G in Ref 2.

bond	O1-Ti	O2-Ti	O3-Ti	O4-Ti
this work	2.18	1.98	2.00	2.12
Ref. 2	2.14	2.04	1.99	2.13

### CBMs of (001) and (101) surface with the adsorption of N<sub>3</sub> molecule

To figure out the nature of the CBMs shown in Fig. 6 and 7, we have calculated the charge densities of these states as shown in Fig. S4b and Fig. S4c. To make a comparison, the total DOS and charge density of the CBM of bulk anatase TiO<sub>2</sub> are also depicted in Fig. S4a. It's clearly seen that the CBM of bulk TiO<sub>2</sub>, extending to the band gap like a tail of conduction band, is provided by *d* orbitals of Ti atoms. In N<sub>3</sub>/(001) system, the CBM is also mainly provided by *d* orbitals of Ti<sub>6c</sub> (six coordinated Ti) atoms. And the states provided by Ti<sub>5c</sub> atoms are lifted to the higher energy levels of conduction bands. However, in N<sub>3</sub>/(101) system, both the *d* orbitals of surface Ti<sub>5c</sub> atoms and bulk Ti<sub>6c</sub> contribute to the CBM. It is concluded that those steep peaks in Fig. 6 and 7 are not real gap states, but parts of the conduction band.

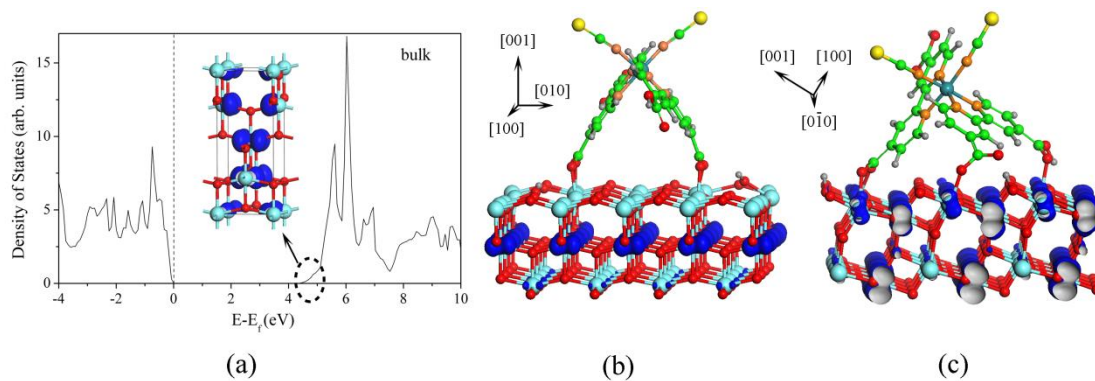


Fig. S4 DOS of the bulk anatase  $\text{TiO}_2$  and its charge density of the CBM (a) and the charge density of CBM of (b) structure B5 and (c) E1. Isodensity values are  $0.02 \text{ e}/\text{\AA}^3$  for (a) and  $0.01 \text{ e}/\text{\AA}^3$  for (b) and (c), respectively.

## Reference

- [1] K. S. Finnie, J. R. Bartlett and J. L. Woolfrey, *Langmuir*, 1998, **14**, 2744–2749.
- [2] F. Schiffmann, J. VandeVondele, J. Hutter, R. Wirz, A. Urakawa and A. Baiker, *J. Phys. Chem. C*, 2010, **114**, 8398–8404.