Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2020

Supporting Information

Effects of interface adsorption configurations on dye-sensitized solar cell performance at the stoichiometric and defected TiO_2 anatase (101): a theoretical investigation

Guang Yang,[a] Guomin Sui,[a] Yuxia Liang,[a] and Xiaodong Xue,[a] Yaqing Feng*[ab] and Bao Zhang*[a]

[a] *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, PR China*
[b] *Tianjin Co-Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, PR China*

Email: baozhang@tju.edu.cn

S1. Computational Results

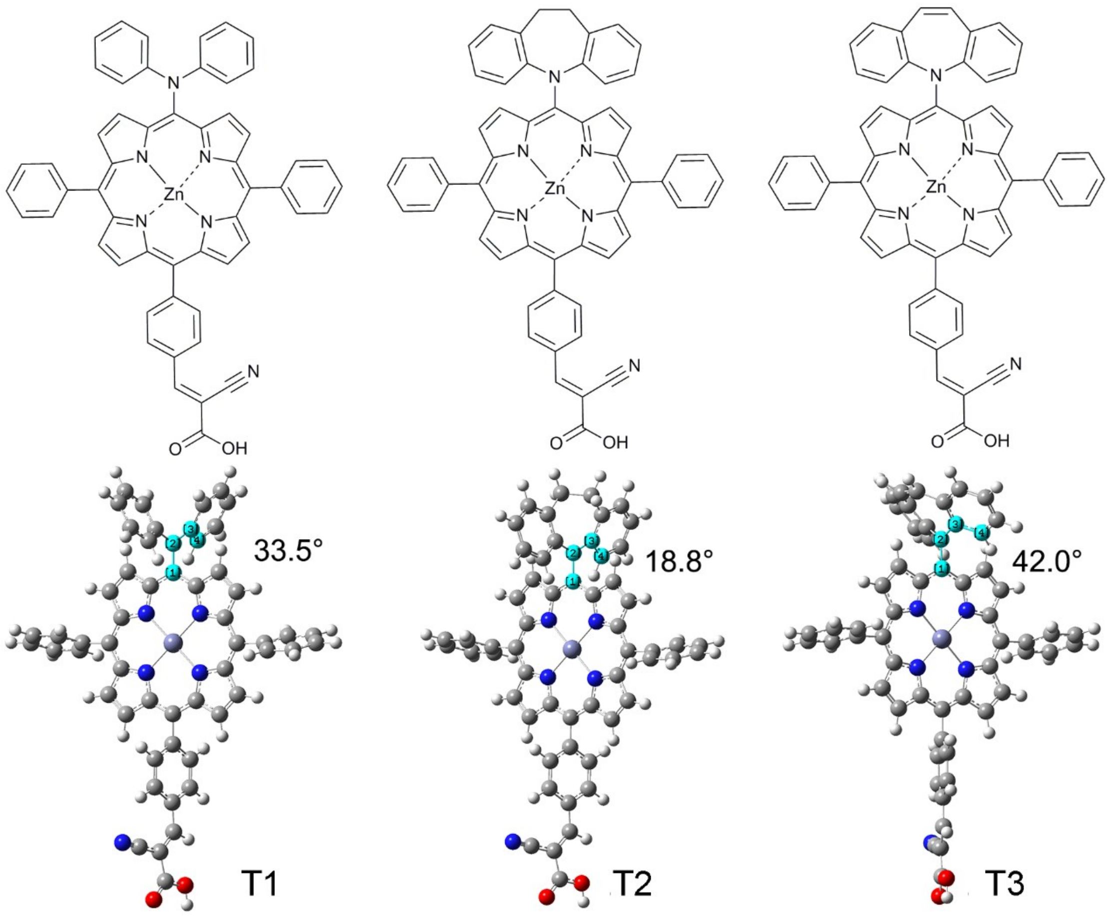

Figure S1. Molecular structures and optimized geometry of ground states of T1-3, with the values showing the dihedral angels of atoms in green.

Table S1. Calculated adsorption configurations of T1-3 and their adsorption energies in three adsorption configurations (D_{NO}, D_N and D_O) on the defected anatase TiO2 (101) surfaces.

Dye	Configurations	Adsorption Energy (eV)	Figures
T1	D_{NO} ($O_{2c\text{-}vac}$, N-Ti_{5c}, O- Ti_{5c})	-1.79	Fig S1 a
	D_N ($O_{2c\text{-}vac}$, N-Ti_{5c})	-1.72	Fig S1 b
	D_O ($O_{2c\text{-}vac}$, O-Ti_{5c})	-1.47	Fig S1 b
T2	D_{NO} ($O_{2c\text{-}vac}$, N-Ti_{5c}, O- Ti_{5c})	-1.77	Fig S1 d
	D_N ($O_{2c\text{-}vac}$, N-Ti_{5c})	-1.71	Fig S1 e
	D_O ($O_{2c\text{-}vac}$, O-Ti_{5c})	-1.44	Fig S1 f
T3	D_{NO} ($O_{2c\text{-}vac}$, N-Ti_{5c}, O- Ti_{5c})	-1.76	Fig S1 g
	D_N ($O_{2c\text{-}vac}$, N-Ti_{5c})	-1.75	Fig S1 h
	D_O ($O_{2c\text{-}vac}$, O-Ti_{5c})	-1.26	Fig S1 i

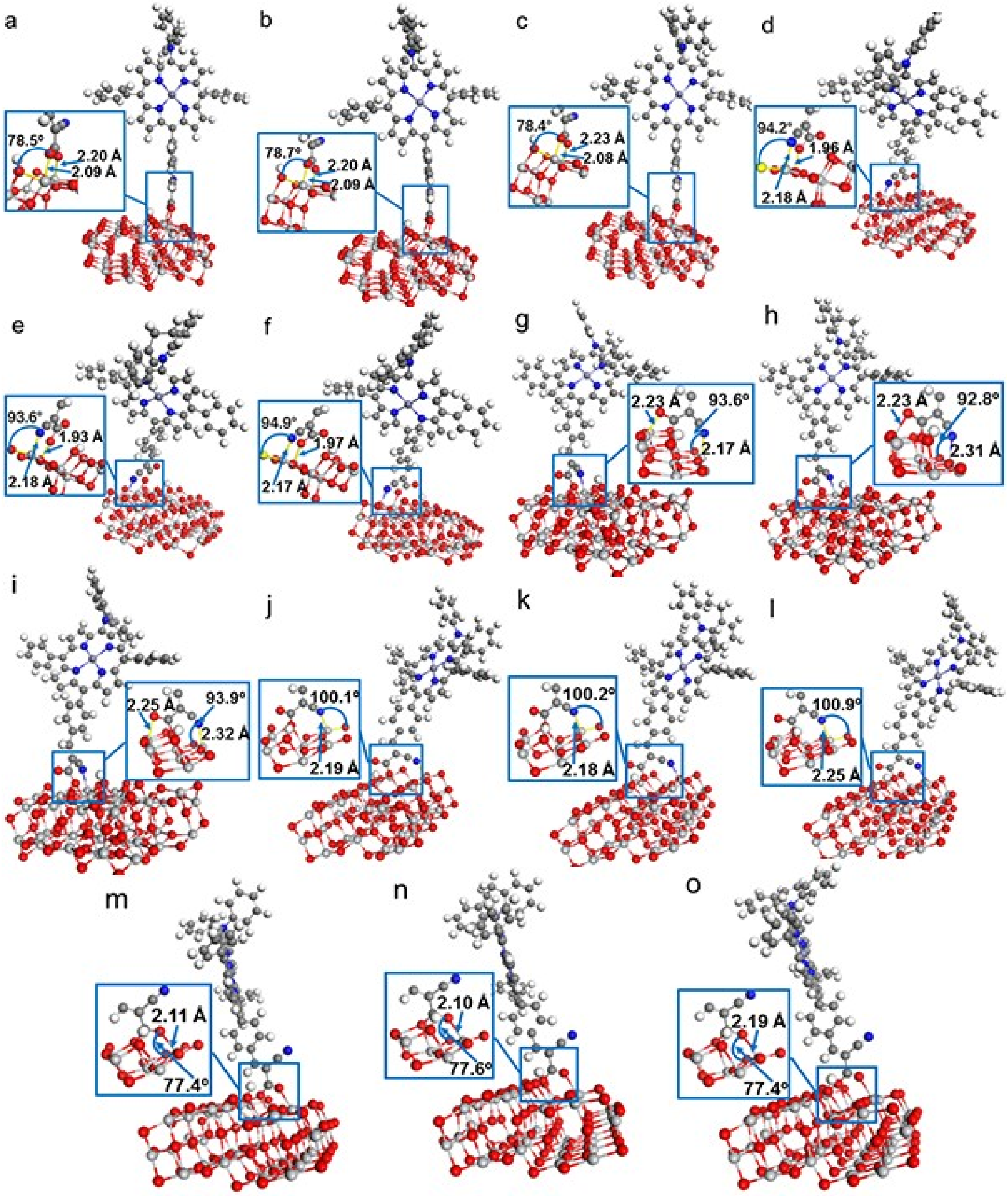

Figure S2. Optimized adsorption configurations of dye T1-3 on the ideal and defected surface. Black, white, red, blue, gray and purple represent C, H, O, N, Ti and Zn atoms respectively. a - c represent the BB mode for T1-3; d - f represent the T mode for T1-3; g - i represent the configurations (D_{NO}) with one O atom in the O_{2c} vacancy and the N and another O atoms at neighboring Ti_{5c} atoms, with the N-Ti distance of 2.31 - 2.32 Å; j - l show the configurations (D_N) with O and N atoms in vacancy and at neighboring T_{5c} atom, with N-Ti distance of 2.18 - 2.25 Å;

m - o present the configurations (D_O) with O-Ti_{5c} bonds of 2.10 – 2.19 Å.

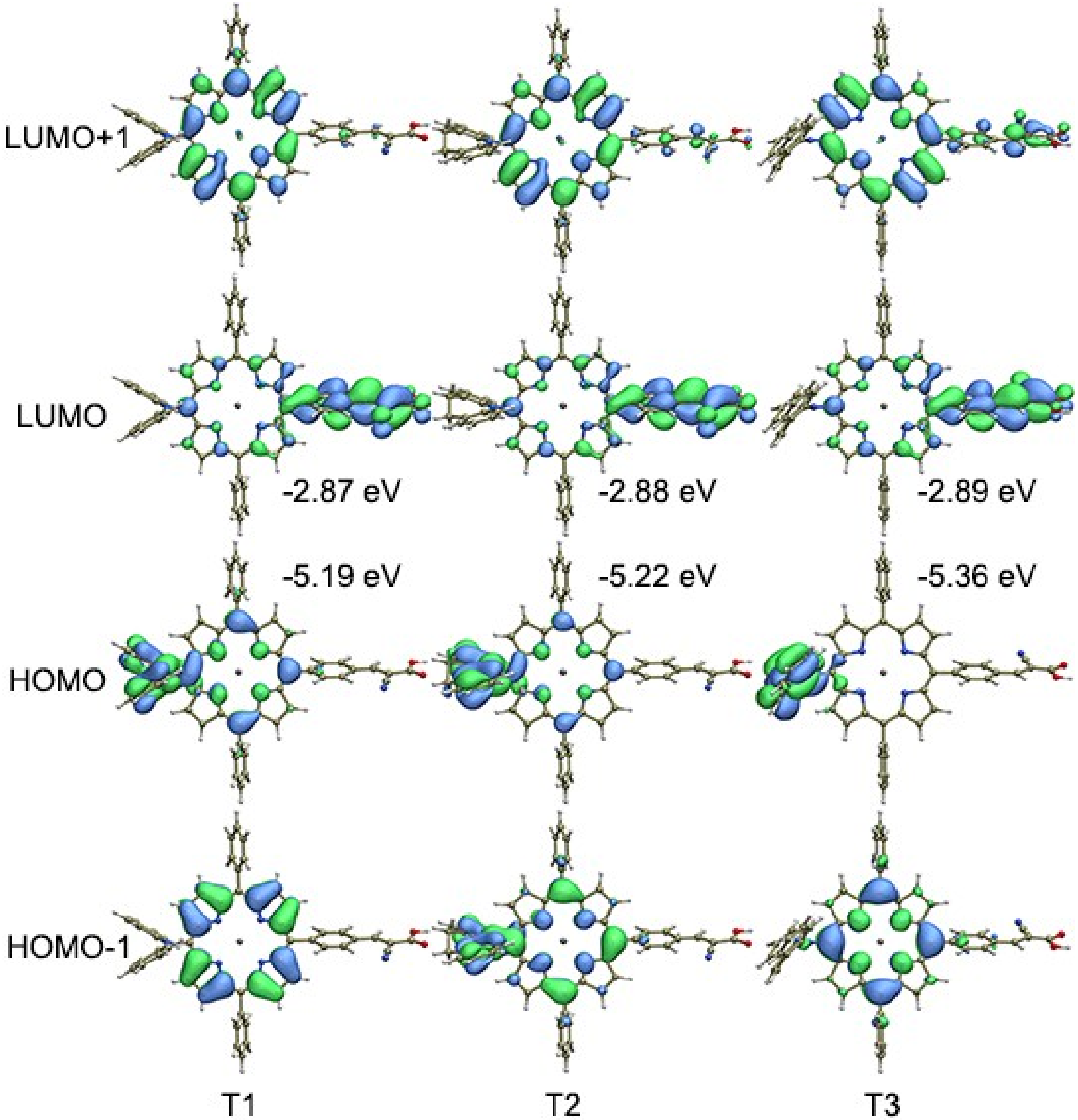

Figure S3. Calculated isosurfaces of the HOMO-1 to LUMO+1 and energy levels of HOMO and LUMO for T1-3.

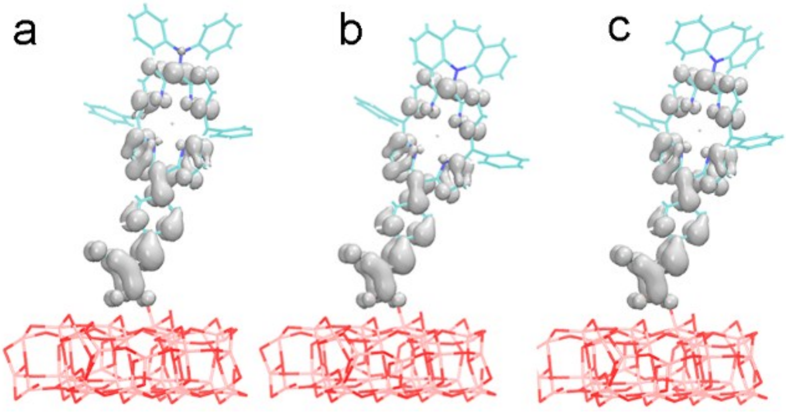

Figure S4. Calculated EH orbitals LUMO for T1-3.

Table S2. Adsorption energy (E_{ads}, eV), of Dye/TiO_2 systems for T1-3 with different adsorption configurations in reduced TiO_2 surface..

Dye	Adsorption Configuration	Adsorption Energy (E_{ads}, eV)
T1	D_{NO}	-1.79
	D_N	-1.72
	D_O	-1.47
T2	D_{NO}	-1.77
	D_N	-1.71
	D_O	-1.44
T3	D_{NO}	-1.76
	D_N	-1.70
	D_O	-1.26

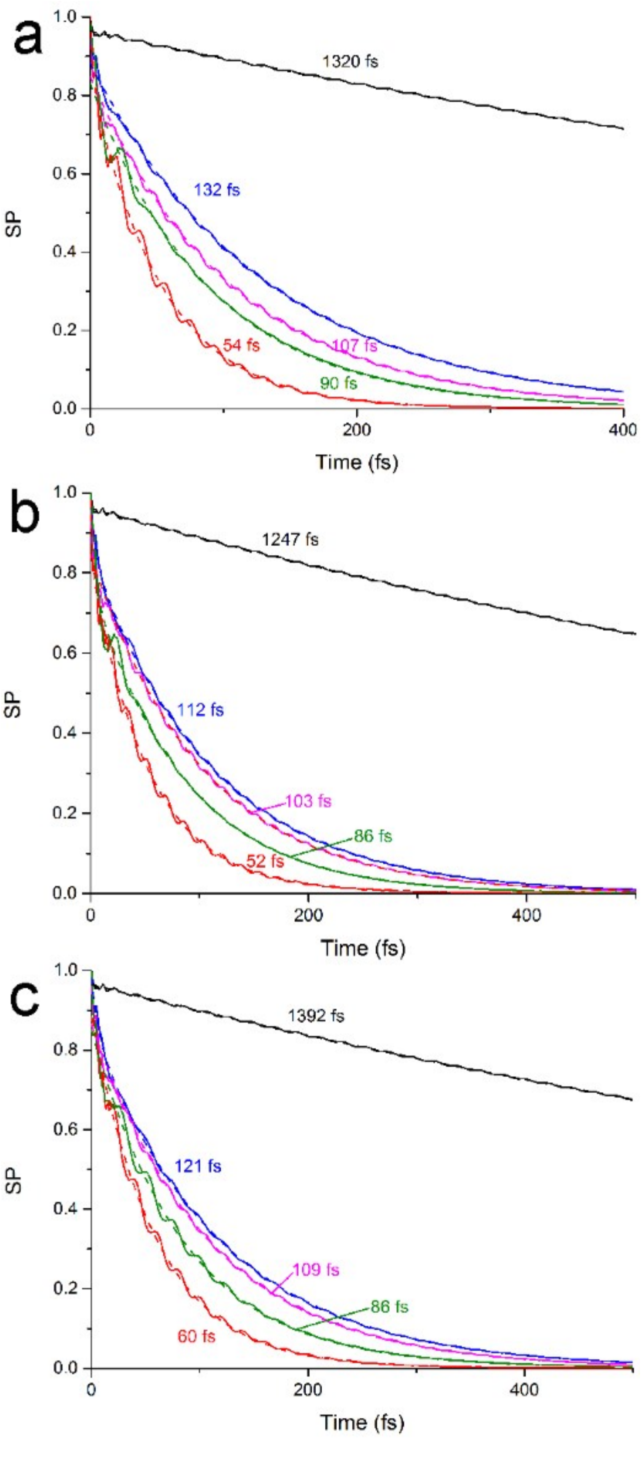

Figure S5. the IET curves (solid line) and exponential fitting (dashed line) from LUMOs orbital of T1 (a), T2 (b) and T3 (c) in adsorption configurations BB (black), D_{NO} (blue), D_N (magenta), D_O (green) and T (red).

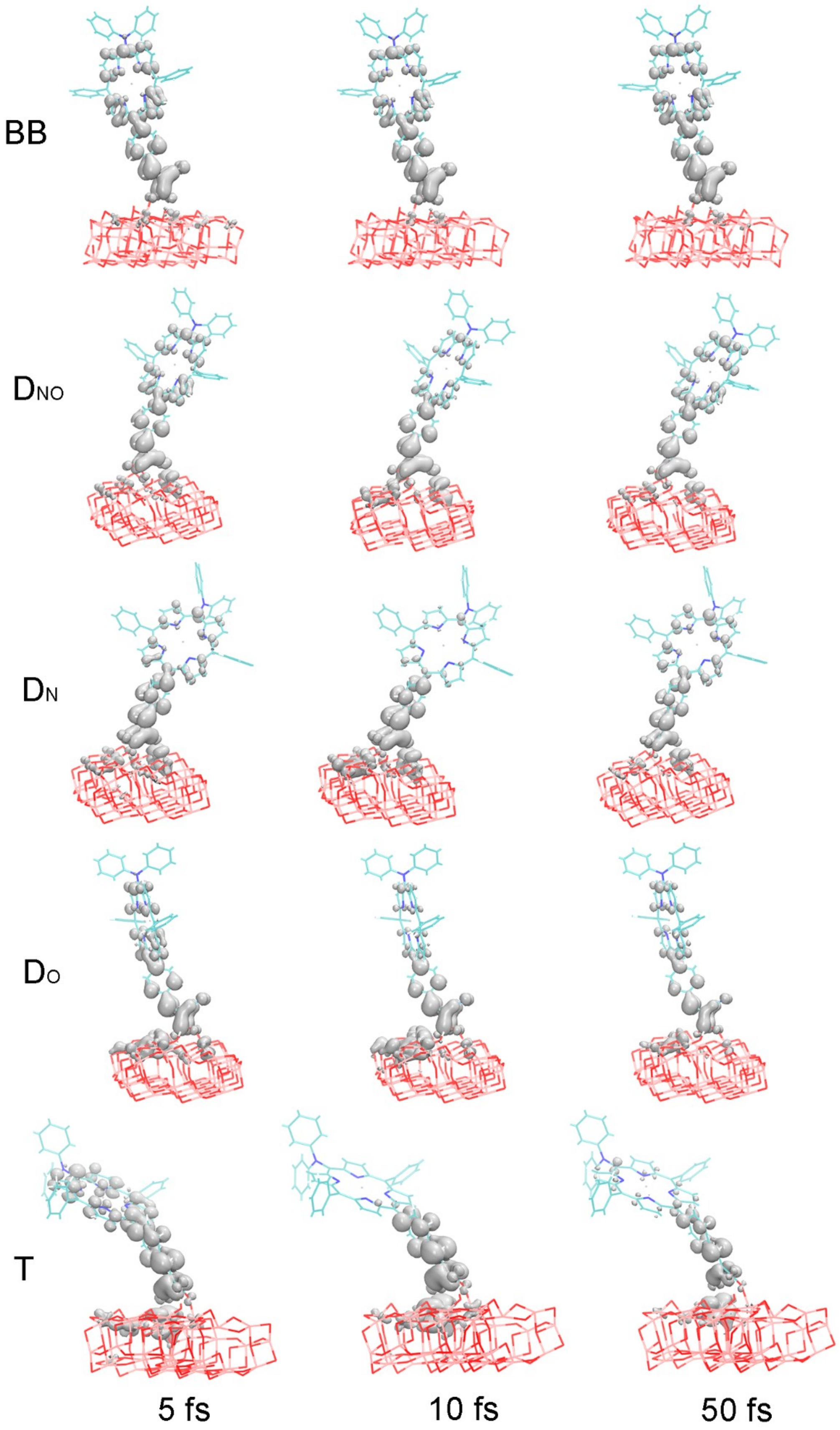

Figure S6. Snapshots of an electronic density isosurface during the evolution of time-dependent charge distribution of T1/TiO_2 system at 5 fs, 10 fs and 50 fs.

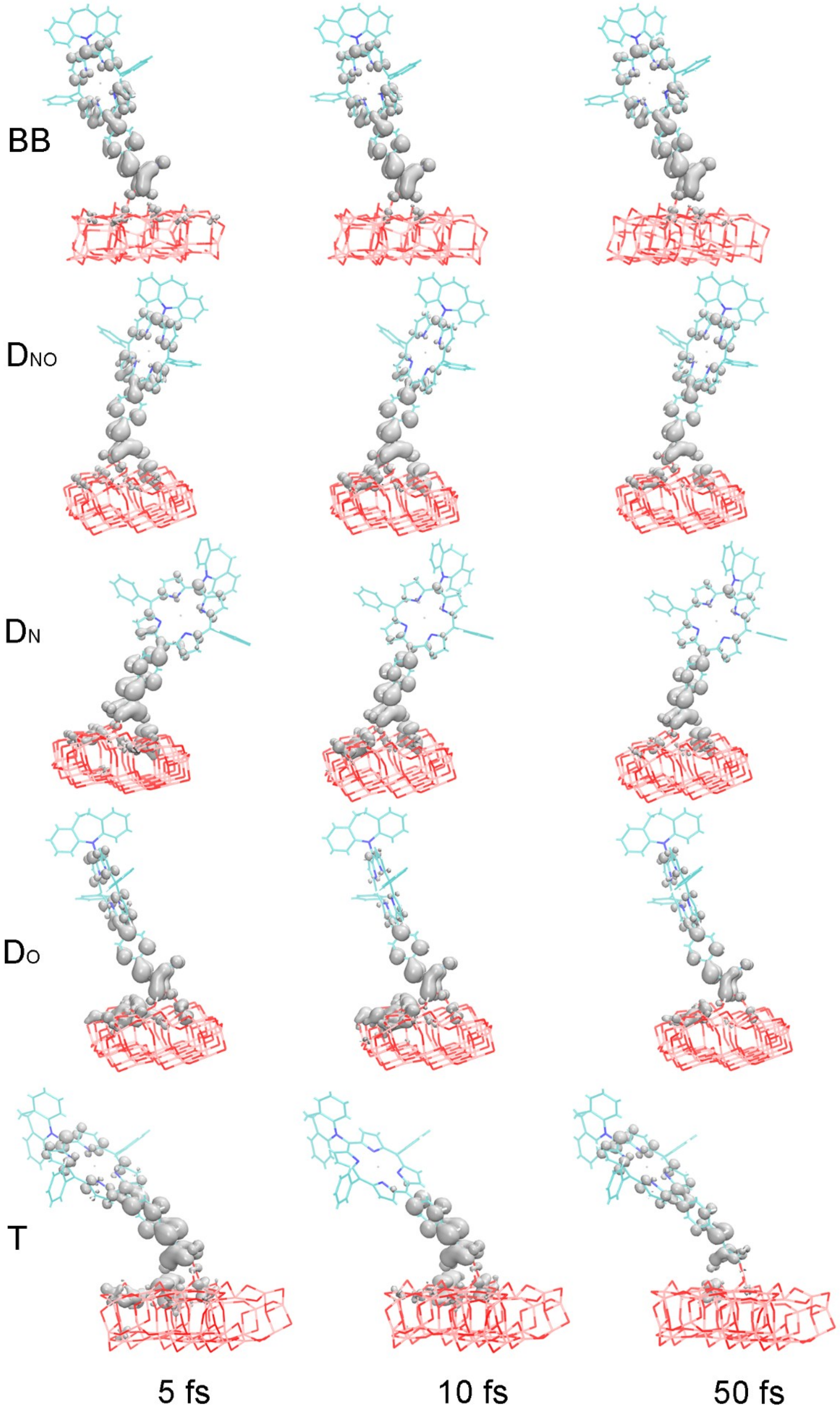

Figure S7. Snapshots of an electronic density isosurface during the evolution of time-dependent charge distribution of T2/TiO_2 system at 5 fs, 10 fs and 50 fs.

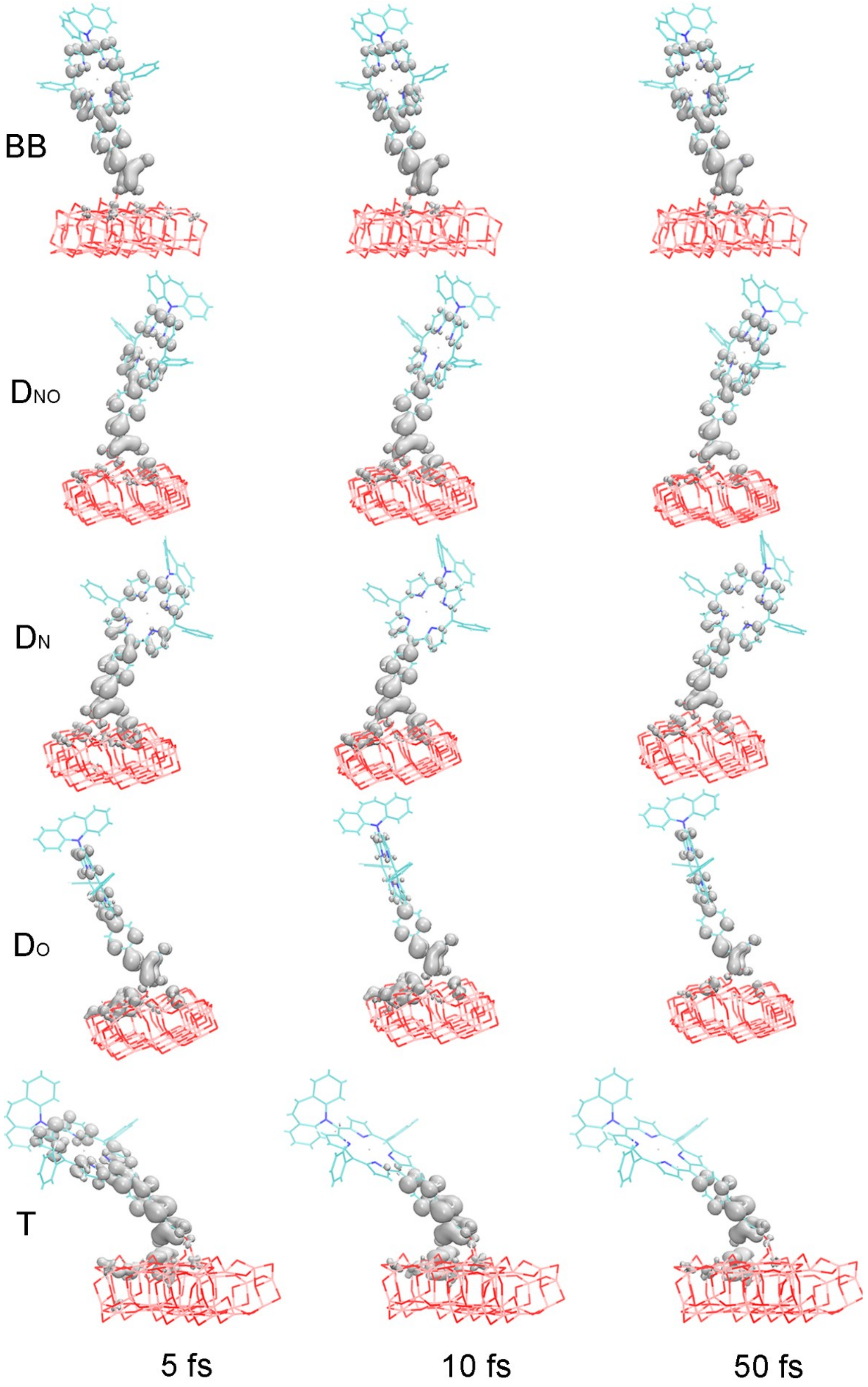

Figure S8. Snapshots of an electronic density isosurface during the evolution of time-dependent charge distribution of T3/TiO_2 system at 5 fs, 10 fs and 50 fs.

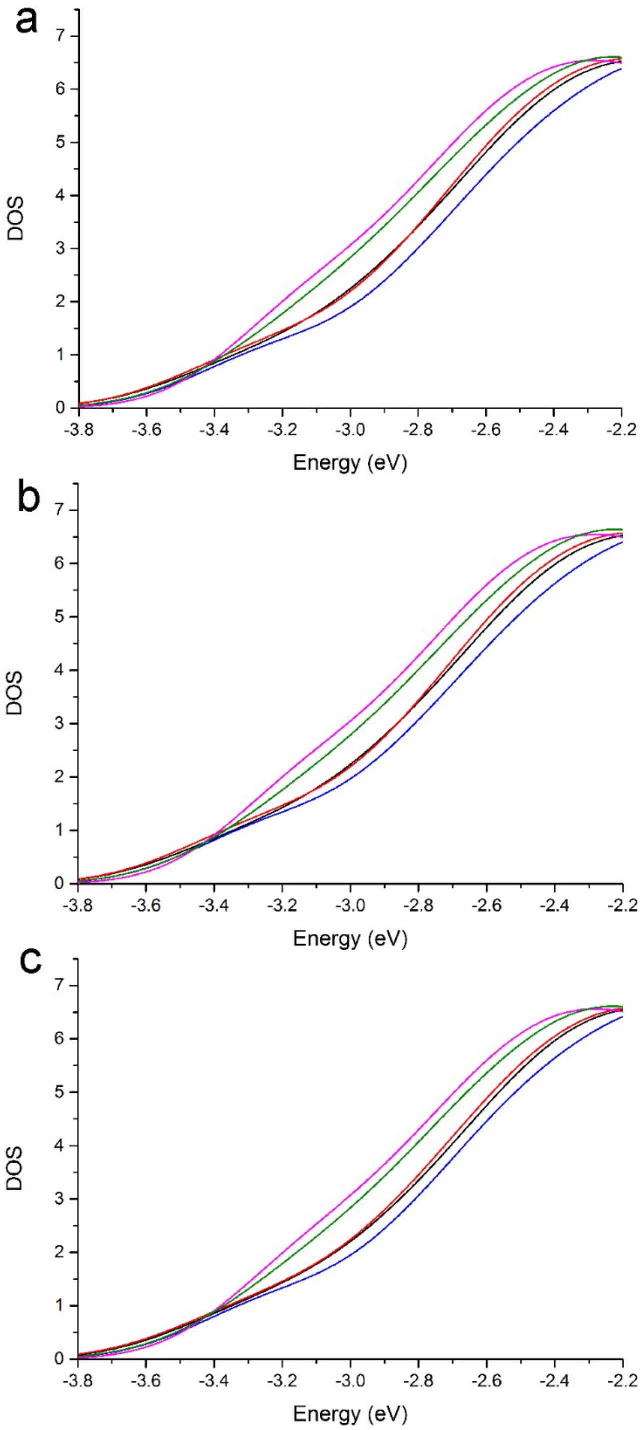

Figure S9 Calculated conduction band PDOS for the TiO_2 of T1 (a), T2 (b) and T3 (c) absorbed on TiO_2 surface with adsorption configurations BB (magenta), T (green), D_N (red), D_{NO} (black), and D_O (blue).

S2. Interfacial Electron Transfer Simulations

The Interfacial Electron Transfer (IET) of dyes on the $(TiO2)_{38}$ cluster with ideal and defected anatase (101) surface was investigated with quantum dynamics simulations using the method developed by Rego and Batista, [1-4] employing the extended Hückel Hamiltonian. IET simulations were performed using IETsim package with a time step of 0.1 fs up to 500 fs on dye/TiO_2 systems. Absorbing potentials were added on the Ti atoms at the bottom layer of TiO_2 to avoid recurrences in electron-transient populations caused by the finite size of the cluster. The brief description of the methodology presented below follows the instruction given by Rego and Batista. [1] The detailed description can be found in ref. 1.

The time-evolved wave function can be written as a linear combination of atomic orbitals (eq 1), where $\left|i,\alpha\right\rangle$ refers to the atomic orbital α of atom i.

$$\left|\Phi(t)\right\rangle = \sum_{i,\alpha} B_{i,\alpha}(t)\left|i,\alpha\right\rangle \tag{1}$$

$B_{i,\alpha}(t)$ in eq 1 is the expansion coefficients, which can be determined according to eq 2 after eq 3 is solved. In eq 3, *H* and *S* represent the EH matrix and the overlap matrix respectively in atomic orbital basis set.

$$B_{i,\alpha}(t) = \sum_{q} Q_{i,\alpha}^{q} C_{q} e^{-(i/\hbar)E_{q}t} \tag{2}$$

$$HQ^{q} = E_{q}SQ^{q} \tag{3}$$

The coefficients C_q in eq 2 are calculated by the initial state expansion in the orthonormal basis set of eigenvectors $\left|q\right\rangle$.

$$\left|\Phi(0)\right\rangle = \sum_{q} C_{q}\left|q\right\rangle \tag{4}$$

The coefficients $Q_{i,\alpha}^{q}$ in eq 2 can be defined according to the expansion of the eigenvectors $\left|q\right\rangle$.

$$\left|q\right\rangle = \sum_{i,\alpha} Q_{i,\alpha}^{q}\left|i,\alpha\right\rangle \tag{5}$$

To investigate the IET process, we calculate survival probability, P(t), which is defined as the probability that the electron is still localized in the adsorbates at time t after excitation (described in eq 6).

$$P(t) = \left|\sum_{i,\alpha}^{MOL}\sum_{j,\beta} B_{i,\alpha}^{*}(t)B_{j,\beta}(t)S_{\alpha,\beta}^{i,j}\right| \tag{6}$$

$S_{\alpha,\beta}^{i,j} = \left\langle i,\alpha \middle| j,\beta\right\rangle$, where α and β denote specific orbitals in atoms i and j. The sum over j atoms includes all the atoms of dye/TiO_2 system, whereas the sum over i atoms excludes the atoms of TiO_2 cluster.

The LUMO orbitals of adsorbates were selected as initial states based on TD-DFT calculation. Approximate characteristic IET times were determined from the exponential fitting to the survival probabilities.

REFERENCES

1 L. G. C. Rego and V. S. Batista, *J. Am. Chem. Soc.*, 2003, **125**, 7989-7997.

2 S. G. Abuabara, L. G. C. Rego and V. S. Batista, *J. Am. Chem. Soc.*, 2005, **127**, 18234-18242.

3 E. Jakubikova, R. C. Snoeberger III, V. S. Batista, R. L. Martin and E. R. Batista, *J. Phys. Chem. A* 2009, **113**, 12532–12540

4 W. R. McNamara, R. C. Snoeberger III, G. Li, J. M. Schleicher, C. W. Cady, M. Poyatos, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig and V. S. Batista, *J. Am. Chem. Soc.*, 2008, **130**, 14329-14338.