

Electronic Supplementary Information

A promising anchor group for efficient organic dye sensitized solar cells with iodine-free redox shuttles: a theoretical evaluation

Ji Zhang[†], Hai-Bin Li[†], Jian-Zhao Zhang, Yong Wu, Yun Geng, Qiang Fu^{*}, Zhong-Min Su^{*}

Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Chang Chun 130024, Jilin, P. R. China.

^{*}Corresponding author: Prof. Qiang Fu; Zhong-Min Su

E-mail: fqiang@nenu.edu.cn; zmsu@nenu.edu.cn;

[†]These authors contributed equally.

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1 Computational details

1.1 Details about the optimization of dye-(TiO₂)₄₈ systems by Siesta

The optimization of dye-(TiO₂)₄₈ systems were performed by means of Siesta ab initio package, which employs norm-conserving pseudopotentials (Troullier–Martins nonlocal form) and localized atomic orbitals as basis set.¹⁻³ Standard DFT using the general gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)⁴ and double- ζ plus polarization (DZP) basis set with an equivalent real-space mesh cutoff 250 Ry were used to optimize the geometries of the studied systems in this work.

1.2 Details for calculating E_{ads}

For molecular adsorption modes (M1-M3) of **1**, E_[dye] is the energy of the dye molecular, and E_[TiO₂] is the energy of the bare TiO₂, while for dissociative adsorption modes (D1-D3) of **1**, E_[dye] is the energy of the dye ion without H proton with the adsorption geometry, and E_[TiO₂] is the energy of the TiO₂ with H proton. All the energies mentioned above were calculated at C-PCM-B3LYP/SVP level of theory in acetonitrile solution.

1.3 Details for assessing ΔE_{CB}

We evaluated the Partial Density of States (PDOS) profiles on TiO₂ at the C-PCM-B3LYP/SVP level of theory to determine the extent of ΔE_{CB} upon the sensitizer adsorption. A linear fit of the low energies profile in a range from 20%-80% of the maximum height was performed and the intercept of this line with x energy axis was taken as CB edge.

1.4 Details about charge displacement curve

The electron density change ($\Delta\rho$) during the formation of the dye-TiO₂ adducts is defined as the density difference between the bound system and its separated fragments at the same position. And the charge displacement (CD) along the z direction defined as:^{5,6}

$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^z \Delta\rho(x, y, z') dz' \quad (1)$$

where $\Delta\rho$ is the electron density difference as defined above. $\Delta q(z)$ measures the electron charge transferred from the right to the left side of the perpendicular plan through z upon formation of the adduct at each point z along the chosen z axis. In our system, two fragments were defined, i.e. the deprotonated dye (negatively charged) and the protonated TiO₂ (positively charged). The CD curve shows the rearrangement of both dye and semiconductor's electron density as a consequence of the dye/surface interaction, and the maximum of the CD curve reflects the charge transferred from the sensitizer to the semiconductor when they have strong interaction.

1.5 Details about the average dye electrostatic potential (V_{EL})

The average dye electrostatic potential on the TiO₂ surface was evaluated by the following relation:⁵

$$V_{EL} = \frac{1}{n_{Ti}} \sum_{i=1}^{n_{Ti}} \sum_{j=1}^{n_q} \frac{q_j}{r_{ij}} \quad (2)$$

where q_j is the j_{th} of the n_q dye point charge. Here we used Merz-Kollman^{7, 8} method to calculate the atomic charge distributions, which has been demonstrated to be the optimal atomic charge model for studying through-space charge-transfer excitations by Jacquemin et al.⁹ And r_{ij} represent the distances between these of charges and each of the titanium atoms in the superficial layer of TiO₂ cluster.

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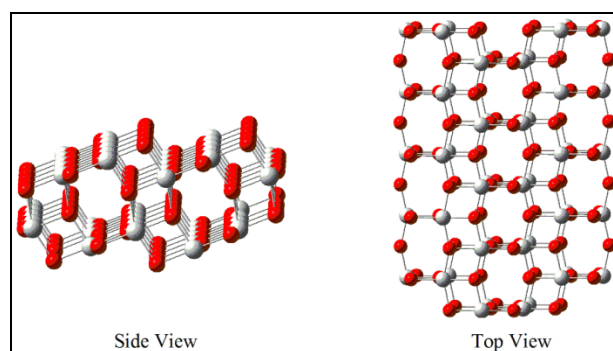


Fig. S1. Initial structure of $(\text{TiO}_2)_{48}$ cluster in side and top view.

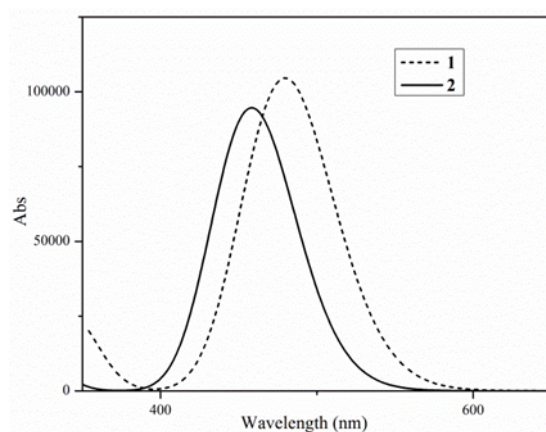


Fig. S2. Calculated absorption spectra of the free organic dyes in CH_2Cl_2 solution at TD-CAM-B3LYP/6-31+G**/B3LYP/6-31G* level of theory.

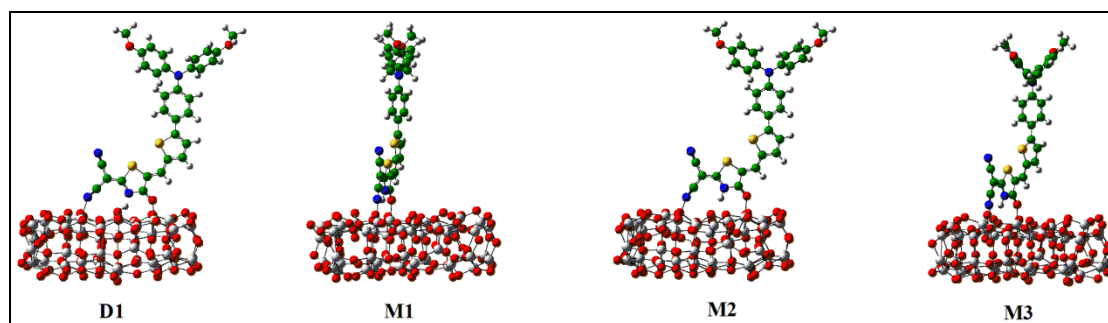


Fig. S3. Optimized geometrical structures of different adsorption modes by Siesta.

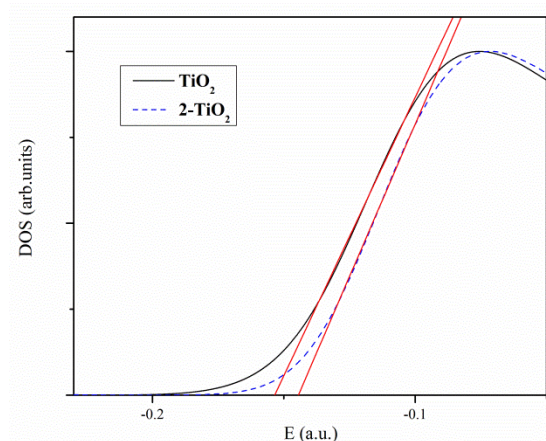


Fig. S4. Total and Partial Density of States (DOS) for **2** adsorbed on $(\text{TiO}_2)_{48}$ cluster. (black solid line) $(\text{TiO}_2)_{48}$ cluster DOS, (blue dash line) PDOS, $(\text{TiO}_2)_{48}$ cluster contribution to the total DOS. The red solid lines intercepts with the energy axis correspond to the calculated CB edges.

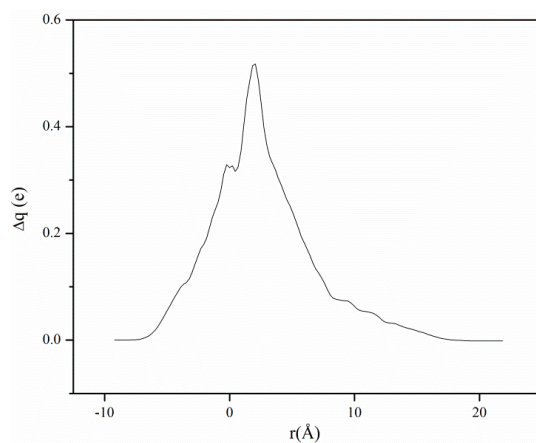


Fig. S5. Charge displacement curve for **1**- $(\text{TiO}_2)_{48}$ in acetonitrile solution under C-PCM-B3LYP/SVP level.

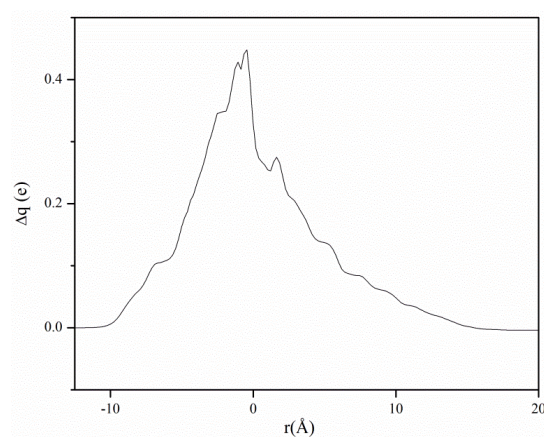


Fig. S6. Charge displacement curve for **2**- $(\text{TiO}_2)_{48}$ in acetonitrile solution under C-PCM-B3LYP/SVP level.

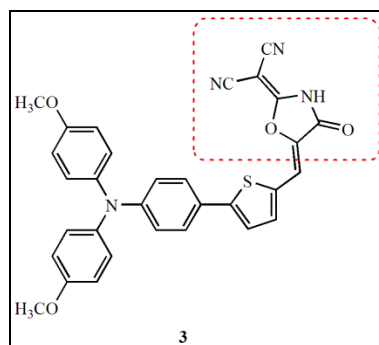


Fig. S7. Molecular structure of **3**.

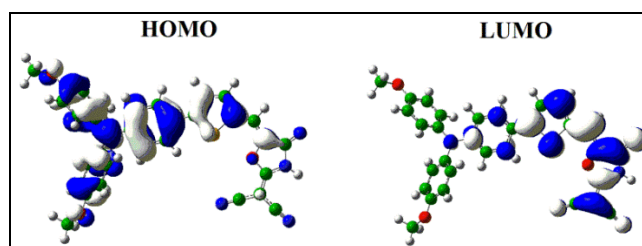


Fig. S8. Frontier molecular orbitals of **3** under TD-CAM-B3LYP/6-31+G(d) level in CH_2Cl_2 with isodensity surface of 0.02 au.

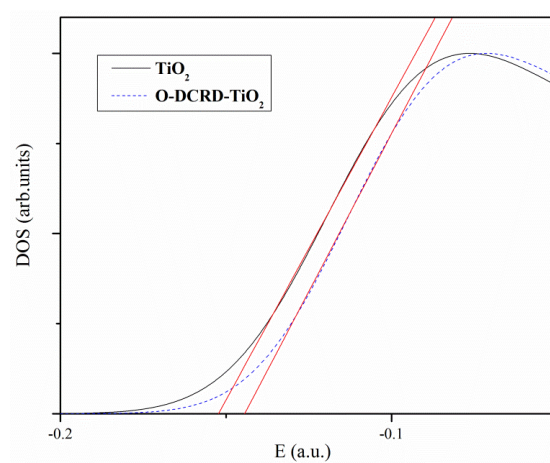


Fig. S9. Total and Partial Density of States (DOS) for **3** adsorbed on $(\text{TiO}_2)_{48}$ cluster. (black solid line) $(\text{TiO}_2)_{48}$ cluster DOS, (blue dash line) PDOS, $(\text{TiO}_2)_{48}$ cluster contribution to the total DOS. The red solid lines intercepts with the energy axis correspond to the calculated CB edges.