Electronic Supplementary Information

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

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1 Computational details

1.1 Details about the optimization of dye-(TiO$_2$)$_{48}$ systems by Siesta

The optimization of dye-(TiO$_2$)$_{48}$ 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-$\zeta$ 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 $I$, $E_{[dye]}$ is the energy of the dye molecular, and $E_{[TiO2]}$ is the energy of the bare TiO$_2$, while for dissociative adsorption modes (D1-D3) of $I$, $E_{[dye]}$ is the energy of the dye ion without H proton with the adsorption geometry, and $E_{[TiO2]}$ is the energy of the TiO$_2$ 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 $\Delta E_{CB}$

We evaluated the Partial Density of States (PDOS) profiles on TiO$_2$ at the C-PCM-B3LYP/SVP level of theory to determine the extent of $\Delta E_{CB}$ 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-TiO$_2$ 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:\textsuperscript{5, 6}

$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{z} \Delta \rho(x, y, z') dz'$$  \hspace{1cm} (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 TiO$_2$ (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 TiO$_2$ surface was evaluated by the following relation:\(^5\)

\[
V_{EZ} = \frac{1}{n_\text{Ti}} \sum_{i=1}^{n_\text{Ti}} \sum_{j=1}^{n_\text{q}} \frac{q_j}{r_{ij}}
\]  

(2)

where \(q_j\) is the \(j\)th of the \(n_\text{q}\) 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.\(^5\) And \(r_{ij}\) represent the distances between these \(j\) charges and each of the titanium atoms in the superficial layer of TiO$_2$ cluster.

Reference

Fig. S1. Initial structure of (TiO₂)_48 cluster in side and top view.

Fig. S2. Calculated absorption spectra of the free organic dyes in CH₂Cl₂ solution at TD-CAM-B3LYP/6-31+G˚/B3LYP/6-31G˚ level of theory.

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

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