Supplementary Information to:

**How dose the Silicon Element Perform in JD-dyes: A Theoretical Investigation**

Li-Na Yang, a Shi-Lu Chen,*a and Ze-Sheng Li* a

*a Key Laboratory of Cluster Science of Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemistry, Beijing Institute of Technology, Beijing 100081, China

Tel: +86 01 6891 8670

E-mail: shlchen@bit.edu.cn (S.-L. Chen), zeshengli@bit.edu.cn (Z.-S. Li)
Computational details

1.1 Details about the light-harvesting efficiency curve

The light-harvesting efficiency (LHE) at the certain wavelength (LHE(λ)) can be calculated according to:¹, ²

\[ \text{LHE}(\lambda) = 1 - 10^{-\varepsilon(\lambda)bc} \]  

(1)

where, \( \varepsilon(\lambda) \) is the molar absorption coefficient at given wavelength, \( b \) is the thickness of TiO\(_2\) film, and \( c \) is the dye concentration on TiO\(_2\) surface. Here, \( b \) and \( c \) are assumed to be 10 µm and 300 mmol L\(^{-1}\), respectively.³-⁵

1.2 Details about the charge displacement curve

The electron density change (Δρ) during the formation of the dye/(TiO\(_2\))\(_{38}\) complexes is defined as the density difference between the dye/(TiO\(_2\))\(_{38}\) complex and the isolated fragments at their geometries after adsorption. And the charge displacement (CD) along the z direction is defined as:\n
\[ \Delta q(z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta \rho(x, y, z) dx dy dz \]  

(2)

where \( \Delta \rho \) is the electron density difference. \( \Delta q(z) \) measures the electron charge transferred from the left to the right 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).

1.3 Details about the calculation of the average dye electrostatic potential (\( V_{\text{EL}} \))

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

(3)

Where \( q_j \) is the \( j^{th} \) of the \( n_{\text{q}} \) dye point charge and \( r_{ij} \) represent the distances of these charges from each of the \( n_{\text{Ti}} \) titanium atoms constituting the superficial layer of the TiO\(_2\) cluster. This quantity represents the effective average electrostatic potential generated by the dye charge distribution in the region of the first semiconductor titanium layer.⁶

References

Figure S1. Absorption spectra of isolated Y1 (black solid line), Y1/(TiO$_2$)$_{38}$ complex (red solid line), isolated Y3 (black dash line), and Y3/(TiO$_2$)$_{38}$ complex (red dash line) dissolved in the CH$_2$Cl$_2$ solution.
Figure S2. Light-harvesting efficiency curves for isolated dyes (solid line) and dye/(TiO$_2$)$_{38}$ complexes (dash line) dissolved in the CH$_2$Cl$_2$ solution.
Figure S3. The frontier molecular orbitals of the investigated dyes.
Figure S4. The molecular orbital distributions of Y1/(TiO₂)₃₈ (a), Y2/(TiO₂)₃₈ (b), and Y3/(TiO₂)₃₈ (c) complexes in the CH₂Cl₂ solution. Blue and yellow indicate to HOMO and LUMO electronic density, respectively. Arrows represent the direction of charge transfer.
Figure S5. Total (DOS) and partial density of states (PDOS) for Y1, Y2, and Y3, respectively, adsorbed onto a (TiO$_2$)$_{38}$ cluster. Black solid line: (TiO$_2$)$_{38}$ cluster DOS. Red solid line: (TiO$_2$)$_{38}$ cluster PDOS with dye adsorbed. Blue solid line: (TiO$_2$)$_{38}$ cluster PDOS with dye-TBA$^+$ co-adsorbed. The intercepts of dash lines with the energy axis correspond to the calculated CB edges.
Figure S6. Isodensity contour plots and charge displacement curves for Y1, Y2, and Y3 adsorbed onto TiO$_2$ in dissociated BB configuration. The red surface identifies the region in which the electron density decreases. The zone of density accumulation is marked by blue.
Figure S7. The structures of JD21-TBA⁺ adducts optimized in the CH₂Cl₂ solution and their relative energies (ΔE is in kcal/mol) calculated at the B3LYP/6-31G(d,p) level.
Figure S8. The structures of Y1-TBA⁺ adducts optimized in the CH₂Cl₂ solution and their relative energies (ΔE is in kcal/mol) calculated at the B3LYP/6-31G(d,p) level.
Figure S9. The optimized geometries of JD21 (a)/Y1 (b)/Y2 (c)/Y3 (d) and TBA$^+$ co-adsorbed systems.
Figure S10. Spin densities for the reduced Y1/(TiO$_2$)$_{38}$ (a), Y2/(TiO$_2$)$_{38}$ (b), Y3/(TiO$_2$)$_{38}$ (c), and oxidized Y1/(TiO$_2$)$_{38}$ (a$'$), Y2/(TiO$_2$)$_{38}$ (b$'$), Y3/(TiO$_2$)$_{38}$ (c$'$) complexes.
Figure S11. Optimized structures for JD21 (a) and Y2 (b) adsorbed on TiO$_2$ nanoparticle.
Figure S12. Structural details of the neutral, reduced, and oxidized dye/(TiO$_2$)$_{38}$ systems.