Supplementary Information to:

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

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## **Computational details**

1.1 Details about the light-harvesting efficiency curve

The light-harvesting efficiency (LHE) at the certain wavelength (LHE( $\lambda$ )) can be calculated according to:<sup>1, 2</sup>

LHE(
$$\lambda$$
) = 1 - 10<sup>- $\varepsilon(\lambda)bc$</sup>  (1)

where,  $\varepsilon(\lambda)$  is the molar absorption coefficient at given wavelength, *b* is the thickness of TiO<sub>2</sub> film, and *c* is the dye concentration on TiO<sub>2</sub> surface. Here, *b* and *c* are assumed to be 10 µm and 300 mmol L-1, respectively.<sup>3-5</sup>

1.2 Details about the charge displacement curve

The electron density change  $(\Delta \rho)$  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: <sup>6-7</sup>

$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{z} \Delta \rho(x, y, z') dz'(2)$$

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<sub>2</sub> (positively charged).

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

$$V_{\rm EL} = \frac{l}{n_{\rm Ti}} \sum_{i=1}^{n_{\rm Ti}} \sum_{j=1}^{n_q} \frac{q_j}{r_{ij}} (3)$$

Where  $q_j$  is the  $j^{th}$  of the  $n_q$  dye point charge and  $r_{ij}$  represent the distances of these charges from each of the  $n_{Ti}$  itianium atoms constituting the superficial layer of the TiO<sub>2</sub> cluster. This quantity represents the effective average electrostatic potential generated by the dye charge distribution in the region of the first semiconductor titanium layer.<sup>7</sup>

References

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## **Supplementary Figures**



**Figure S1.** Absorption spectra of isolated Y1 (black solid line), Y1/(TiO<sub>2</sub>)<sub>38</sub> complex (red solid line), isolated Y3 (black dash line), and Y3/(TiO<sub>2</sub>)<sub>38</sub> complex (red dash line) dissolved in the CH<sub>2</sub>Cl<sub>2</sub> solution.



**Figure S2.** Light-harvesting efficiency curves for isolated dyes (solid line) and dye/(TiO<sub>2</sub>)<sub>38</sub> complexes (dash line) dissolved in the CH<sub>2</sub>Cl<sub>2</sub> solution.



Figure S3. The frontier molecular orbitals of the investigated dyes.



**Figure S4**. The molecular orbital distributions of  $Y1/(TiO_2)_{38}$  (a),  $Y2/(TiO_2)_{38}$  (b), and  $Y3/(TiO_2)_{38}$  (c) complexes in the CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>)<sub>38</sub> cluster. Black solid line: (TiO<sub>2</sub>)<sub>38</sub> cluster DOS. Red solid line: (TiO<sub>2</sub>)<sub>38</sub> cluster PDOS with dye adsorbed. Blue solid line: (TiO<sub>2</sub>)<sub>38</sub> cluster PDOS with dye-TBA<sup>+</sup> 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<sub>2</sub> 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<sup>+</sup> adducts optimized in the  $CH_2Cl_2$  solution and their relative energies ( $\Delta E$  is in *kcal*/mol) calculated at the B3LYP/6-31G(d,p) level.



**Figure S8**. The structures of Y1-TBA<sup>+</sup> adducts optimized in the  $CH_2Cl_2$  solution and their relative energies ( $\Delta E$  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<sup>+</sup> co-adsorbed systems.



**Figure S10**. Spin densities for the reduced Y1/(TiO<sub>2</sub>)<sub>38</sub> (a), Y2/(TiO<sub>2</sub>)<sub>38</sub> (b), Y3/(TiO<sub>2</sub>)<sub>38</sub> (c), and oxidized Y1/(TiO<sub>2</sub>)<sub>38</sub> (a`), Y2/(TiO<sub>2</sub>)<sub>38</sub> (b`), Y3/(TiO<sub>2</sub>)<sub>38</sub> (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.