Electronic Supplementary Information

The effect of D-[D_e-π-A]$_n$ (n = 1, 2, 3) type dyes on overall performance of DSSC: a theoretical investigation

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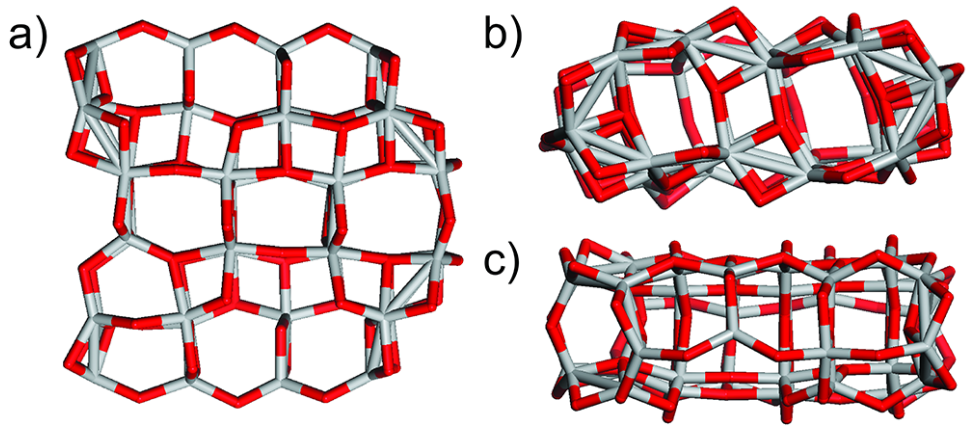

Fig. ESI-1 The cluster model of $(TiO_2)_{38}$ (101) surface: a) Top view; b) Front view; c) side view.

In order to insight into the dye@TiO_2 interaction, a large $(TiO_2)_{38}$ (114 atoms) cluster with exposing the majority (101) surface is constructed comprising two layers of Ti and O atoms. This model is enough to neglect molecular interactions between the periodic replicas and applied widely in many previous investigations as shown in Fig. ESI-1.

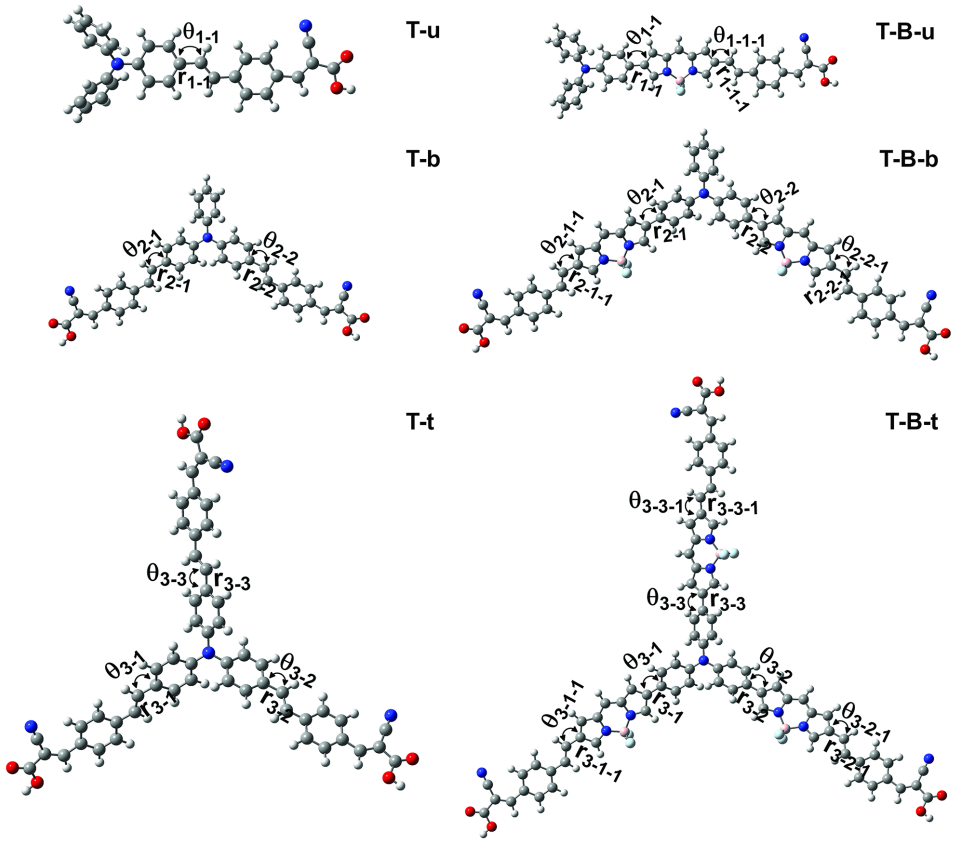

Fig. ESI-2 Optimized structures of the dyes without extra donor groups and the dyes with inserting *B* groups.

With the aim of investigating the effect of D-[D_e-π-A]$_n$ (n = 1, 2, 3) type dyes on the performance of DSSC device, some selected geometrical parameters are listed in Fig. ESI-2. In current work, since the labels for dyes with *Pe* and *Ph* groups are same as the dyes with *B* group, for clarity, we just present the labels for following two cases.

Table. ESI-1 Calculated the charge transfer parameters of dyes (q_{ct} in unit of e, D_{ct} ,H, and t in unit of Å).

dyes	q_{ct}	D_{ct}	H	t
T-u	0.858	5.657	5.415	0.242
T-b	0.771	2.516	7.307	-4.791
T-t	0.835	4.339	7.757	-3.418
T-B-u	0.978	6.162	6.117	0.045
T-B-b	0.870	2.707	7.597	-4.890
T-B-t	0.981	5.894	8.434	-2.540
T-Pe-u	0.875	7.284	7.275	0.009
T-Pe-b	0.888	1.225	13.035	-11.810
T-Pe-t	0.948	4.357	13.034	-8.677
T-Ph-u	1.166	8.595	7.523	1.072
T-Ph-b	1.189	0.061	12.901	-12.840
T-Ph-t	1.366	10.496	10.602	-0.106

The calculated ICT parameters are collected in Table. ESI-1.

Multi-branches complicate the transition character. Several frontier molecular orbitals are illustrated in Fig. ESI-3 to help understand the absorption nature.

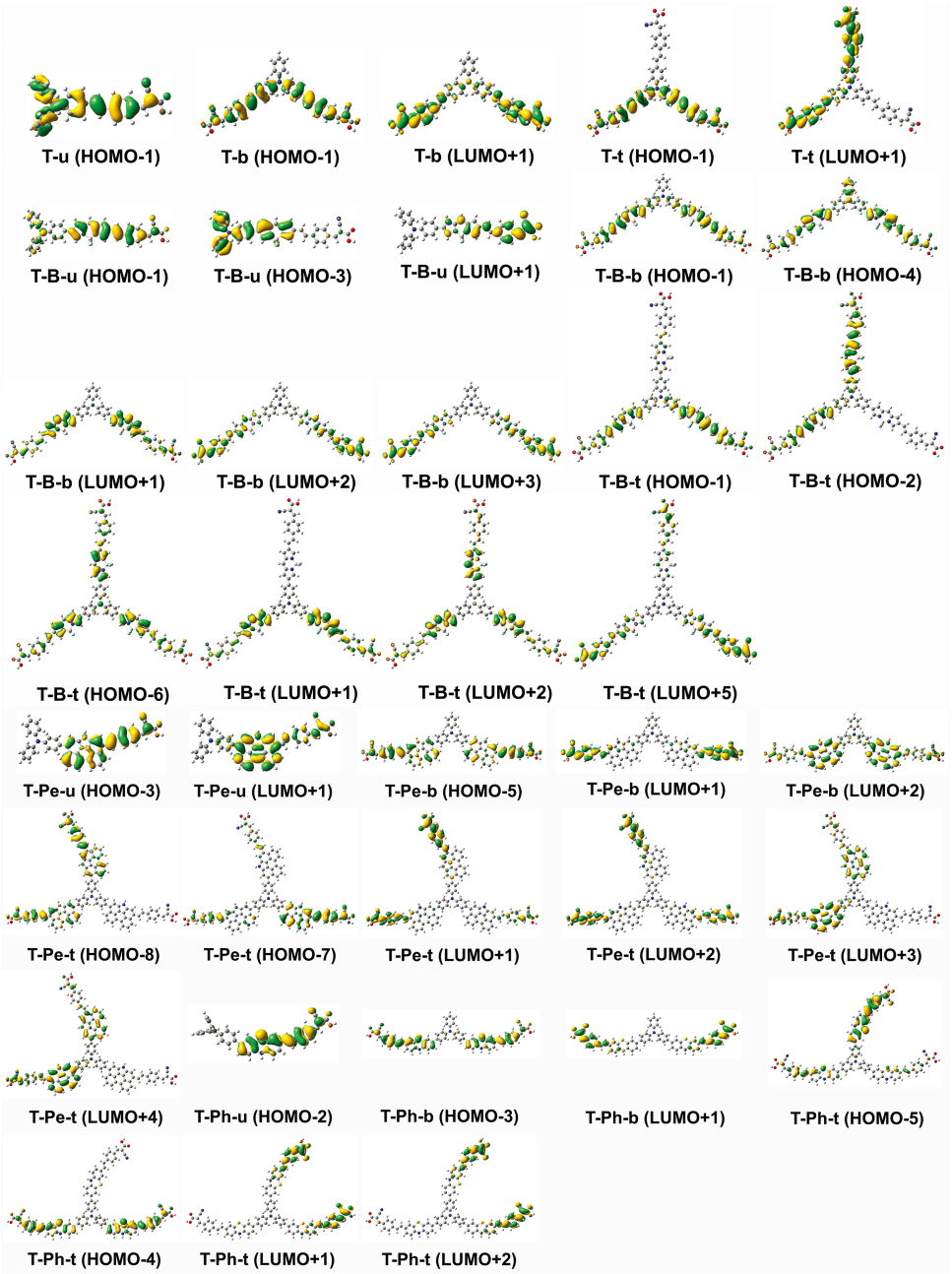

Fig. ESI-3 Frontier molecular orbitals involved in vertical transition.

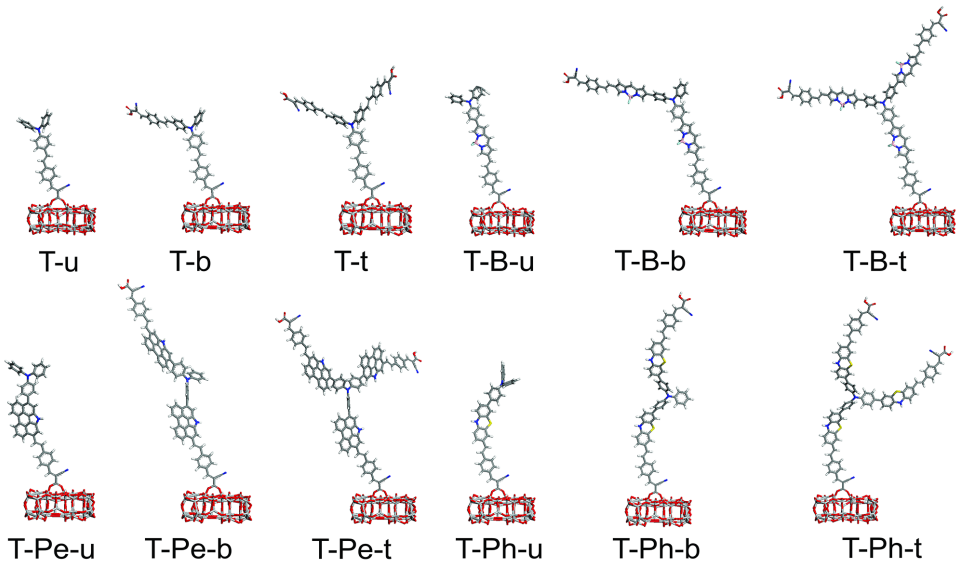

Fig. ESI-4 The optimized dye@TiO_2 interface geometries (side view).

As depicted in Fig. ESI-4, all the geometries of dye@$(TiO_2)_{38}$ are presented, for the convenience of discussion the effect of multi-branches, we only use one anchor group absorbed onto TiO_2 surface to avoid the multi-anchor groups' impact.

DSSC is a device that is applied to convert the excited electrons into electricity current. If more photons were captured, there would be more electrons to be excited, further lead to more electrons being injected into the TiO_2, and finally increases the short-circuit current density (J_{sc}) of solar cell. J_{sc} is related to the integral photon flux density ($\Phi(\lambda)$) in the whole absorption coverage. The $\Phi(\lambda)$ is defined as the number of photons per second per unit area and per unit wavelength, it can be estimated by following expression at given wavelength (λ),

$$\Phi(\lambda) = P(\lambda)/E \tag{1}$$

thus, the total photon number per second per unit area within the whole spectrum coverage can be calculated by the following equation:

$$\int \Phi(\lambda) \cdot d\lambda = \int (P(\lambda)/E) \cdot d\lambda \tag{2}$$

where,

- $P(\lambda)$, the spectral power density in W m^{-2} m^{-1};
- E, the energy of photon at the wavelength of light (λ).

The E can be expressed as:

$$E = (h \cdot c)/\lambda \tag{3}$$

where,

- h, the Planck's constant, 6.626 $\times$ 10^{-34} J s;
- c, the speed of light, 3.0 $\times$ 10^{8} m s^{-1}.

Moreover, the maximal photon generated current (J_{ph}) can be estimated as:

$$J_{ph} = q \int \Phi(\lambda) \cdot d\lambda \tag{4}$$

where,

- q, the elementary charge, 1.6×10^{-19} C.

here, the flow of electric charge across a surface per second per unit area in whole spectrum that is equal to the maximum short circuit density (J_{sc}^{max}) the cell can produced.

On the one hand, the sun irradiance in experiment is too complicated to be expressed within a simple formula; on the other hand, the spectral irradiance of sun is well approximated by the emission of a blackbody at temperature of about 5778 K[1]. Therefore, the power density at the given wavelength can be rewritten as:

$$P(\lambda) = (R/D)^2 2\pi hc^2/[\lambda^5(e^{hc/(k\lambda T)} - 1)] \tag{5}$$

where,

- R, the radius of sun, 0.695×10^9 m;
- D, the distance from sun to earth, 1.496×10^{11} m;
- k, Boltzmann's constant, $1.3806488 \times 10^{-23}$ J K^{-1};
- T, temperature of blackbody. Here, $T = 5778$ K.

In fact, the radiation absorbed by sensitizers is not absolutely complete, with the consideration of the practical condition, we introduce $\eta_{LHE}(\lambda)$ for gaining the real absorption. Therefore, the exact part of photon flux density ($\Phi(\lambda)$) generated by sensitizers per second per unit area at the given wavelength (λ) can be expressed as the following.

$$\begin{aligned} \Phi(\lambda) &= (R/D)^2 \eta_{LHE}(\lambda) 2\pi c/[\lambda^4(e^{hc/(k\lambda T)} - 1)] \\ &= 40682.5 \times \frac{1 - 10^{-\Gamma\sigma(\lambda)}}{\lambda^4(e^{2.49\times10^{-6}/\lambda} - 1)} \end{aligned} \tag{6}$$

The maximal photon generated current (J_{ph}) can be estimated as:

$$J_{ph} = q \int 40682.5 \times \frac{1 - 10^{-\Gamma\sigma(\lambda)}}{\lambda^4(e^{2.49\times10^{-6}/\lambda} - 1)} \cdot d\lambda \tag{7}$$

Since the flow of electric charge across a surface per second per unit area in whole spectrum that is equal to the maximum short circuit density (J_{sc}^{max}) the cell can produced, thus, we can evaluate the J_{sc} based on the results of J_{ph}.

References

[1] W. Guo-sheng, W. Teng, W. Zheng-wen, L. Shu-ping, Study on temperature characteristics of solar cells, Telecom Power Technology 1 (2013) 007.