Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Theoretical insight into the influence of different molecular design strategies on photovoltaic properties for a series of POM-based dyes applied in dye-sensitized solar cells

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1. Theoretical background

The power conversion efficiency (η) of DSSCs can be expressed as [1]:

$$\eta = FF\frac{V_{OC}J_{SC}}{I_S} \quad (1)$$

where I_S is the intensity of the incident light and FF is the fill factor of the cell. The J_{SC} can be defined as follows:

$$J_{SC} = \int LHE(\lambda)\Phi_{inject}\eta_{collect}I_S(\lambda)d\lambda \quad (2)$$

where $LHE(\lambda)$, the light harvesting efficiency at a specific wavelength, is determined by $LHE(\lambda) = 1 - 10^{-f}$ and f is the oscillator strength of dyes corresponding to the maximum absorption λ_{max}. $\eta_{collect}$ is the charge collection efficiency, which is assumed to be a constant for the same DSSCs. Φ_{inject} is the electron injection efficiency, which is closely connected with k_{inj}, and can be described as follows [2]:

$$k_{inj} = \frac{2\pi}{h} V_{DA}^2 \left(\frac{\pi}{\chi K_B T}\right)^{1/2} \exp\left[-\frac{(\Delta G_{inj} + \chi)}{4\chi K_B T}\right]$$

where V_{DA} is the coupling between the donor and acceptor states and χ is the reorganization energy. ΔG_{inj} can be determined by the following equation [3]:

$$\Delta G_{inj} = E^*_{dye} - E_{CB} \quad (3)$$

where E^*_{dye} is the oxidation potential of dye in the excited state, which is related to the oxidation potential of the dye in the ground state (E_{dye}) and the vertical transition energy (E_v), i.e., $E^*_{dye} = E_{dye} - E_v$ [3]. E_{CB} is the reduction potential of the TiO_2 conduction band (CB) and the experimental value –4.00 eV (vs vacuum) is used [4]. χ can be obtained using the following formula:

$$\chi = [E_0^+ - E_+] + [E_+^0 - E_0] \quad (4)$$

Where E_0^+ is the energy of the cation calculated based on the optimized structure of

the neutral molecule, E_+ represents the energy of the cation calculated based on the optimized cation structure, E_+^0 corresponds to the energy of the neutral molecule calculated at the cationic state and E_0, is the energy of the neutral molecule at the ground state.

In order to evaluate the ICT abilities of dyes, the ICT parameters including the amount of transferred charges (q^{CT}), the corresponding effective charge transfer distance (d^{CT}) and the t index that assess the degree of separation between ρ^+ (r) and ρ^- (r) based on the total densities for ground and excited states were calculated [5,6]. ρ^+ (r) and ρ^- (r) are defined as the points in space where the density increment and depletion upon absorption are produced. The larger t is, the little overlap between the electron density depletion and increment regions exists. The difference of electronic densities related to the electronic transition is given by:

$$\Delta\rho\ (r) = \rho_{ES}\ (r) - \rho_{GS}\ (r) \tag{5}$$

ρ_{ES} (r) and ρ_{GS} (r) are proposed to represent the electronic densities of excited and ground states, respectively. ρ^+ (r) and ρ^- (r) are defined as the points in space where the density increment and depletion upon absorption are produced. And q^{CT} can be proposed:

$$q^{CT} = \int \rho^+\ (r)\ \mathrm{d}r \tag{6}$$

The barycenters (r^+ and r^-) of density distributions defined by ρ^+ (r) and ρ^- (r) are written as the following equations:

$$r^+ = (x^+, y^+, z^+) = 1/q^{CT} \int r\rho^+\ (r)\ \mathrm{d}r \tag{7}$$

$$r^- = (x^-, y^-, z^-) = 1/q^{CT} \int r\rho^-\ (r)\ \mathrm{d}r \tag{8}$$

The difference between r^+ and r^- is defined as d^{CT}.

To elucidate the intrinsic reasons of different interaction energy (ΔE_{tot}) for the dimers of dyes, simple energy decomposition analysis (EDA) was performed. ΔE_{tot} can be decomposed as [7]:

$$\Delta E_{tot} = (\Delta E_{els} + \Delta E_{ex}) + \Delta E_{orb} = \Delta E_{steric} + \Delta E_{orb} \quad (9)$$

where ΔE_{els} is electrostatic interaction term, and normally negative if two fragments are neutral; ΔE_{ex} is exchange repulsion term, which comes from the Pauli repulsion effect and is invariably positive. For convenience, ΔE_{els} and ΔE_{ex} terms are usually combined as steric term (ΔE_{steric}). ΔE_{orb} is orbital interaction term, which arises from the mix of occupied molecular orbital (MOs) and virtual MOs. If the combined wavefunction is used as initial guess for complex, then E_{orb} can be evaluated by subtracting the first SCF iteration energy from the last SCF iteration energy:

$$\Delta E_{orb} = E_{SCF,\,last} - E_{SCF,\,1st} \quad (10)$$

$$\Delta E_{steric} = \Delta E_{els} + \Delta E_{ex} = \Delta E_{tot} - \Delta E_{orb} \quad (11)$$

As for $V_{OC,}$ it can be defined by [8]:

$$V_{OC} = \frac{E_{CB}}{q} + \frac{kT}{q}\ln\left(\frac{n_c}{N_{CB}}\right) - \frac{E_{redox}}{q} \quad (12)$$

where n_c is the number of electrons in CB, while q and kT are constants, representing the unit charge and thermal energy, respectively. N_{CB} represents the accessible density of CB states. The dye absorbed on TiO_2 surface can lead to the energy shift of E_{CB} (ΔE_{CB}). Apparently, a dye with large n_c and ΔE_{CB} will induce a significant increase of V_{OC}.

2. The multicenter bond index

The multicenter bond index is a measure of aromaticity, and the higher the number, the stronger the aromaticity. The multicenter bond index is defined as:

$$I_{\mathrm{ABCDEF...K}} = \sum_{a\in A}\sum_{b\in B}\sum_{c\in C}\cdots\sum_{k\in K}[(PS)_{ab}(PS)_{bc}(PS)_{cd}\cdots](PS)_{ka} \quad (13)$$

where P is the single electron density matrix, S is the overlapping matrix, a, b, c... are the number of the basis function, A, B, C... represent the number of atoms in the ring, and the atoms are adjacent according to their connection in the ring.

3. Simulations of the electron injection

The time-dependent survival probabilities (TDSP) curves were defined as the probability of the photo-excited electron which is still in the adsorbed dye molecule at time *t*. Therefore, the TDSP can be computed by applying the time-evolved electronic wave function into the atomic orbitals of the adsorbed dye molecule.

The time-evolved wave function $\varphi(t)$ can be written as a linear combination of atomic orbitals:

$$\varphi(t) = \sum_{i,j} B_{i,j}(t)\,\phi_{i,j} \quad (14)$$

where $\phi_{i,j}$ represents the orbitals *j* of the *i*-th atom. The expansion coefficients $B_{i,j}(t)$, introduced in Eq. (13), can now be computed according to the follow equation:

$$B_{i,j}(t) = \sum_{k} Q^{k}_{i,j}\, C_k exp(-\frac{i}{\hbar} E_k t) \quad (15)$$

The coefficient C_k in Eq. (14) is defined by the expansion of the initial state in an orthonormal basis set of $\phi(k)$,

$$\varphi(0) = \sum_{k} C_k\,\phi(k) \quad (16)$$

The coefficient $Q^{k}_{i,j}$ in this equation is defined according to the expansion of $\phi(k)$ as

a linear combination of the atomic orbitals:

$$\phi(k) = \sum_j Q_j^k \phi_j \tag{17}$$

The eigenvalue E_k in Eq. (14) can be obtained by solving the extend Hückel theory (EH) eigenvalue problem:

$$HQ^k = E_k S Q^k \tag{18}$$

where H is the EH matrix and S is the overlap matrix in the atomic orbital basis. The non-diagonal Hamiltonian matrix is here determined by the Wolfsberg-Helmholtz constant K and the overlapping matrix element:

$$H_{j,m} = K S_{jm} \frac{H_{jj} + H_{mm}}{2} \tag{19}$$

Usually, the constant K is set to be 1.75, and the S_{jm} is defined according to the overlap of the atomic orbitals:

$$S_{jm} = \langle \varphi_j | \varphi_m \rangle \tag{20}$$

Therefore, the projection of the time-evolved electronic wave function onto the atomic orbitals of the adsorbed dye molecular can be obtained as follows:

$$\rho_{MOL}(t) = |\sum_j^{MOL} \sum_m B_j^*(t) B_m(t) S_{jm}| \tag{21}$$

Note that the sum over m includes all of the atoms in the research object, whereas the sum over j only includes the atoms in the adsorbed dye molecular.

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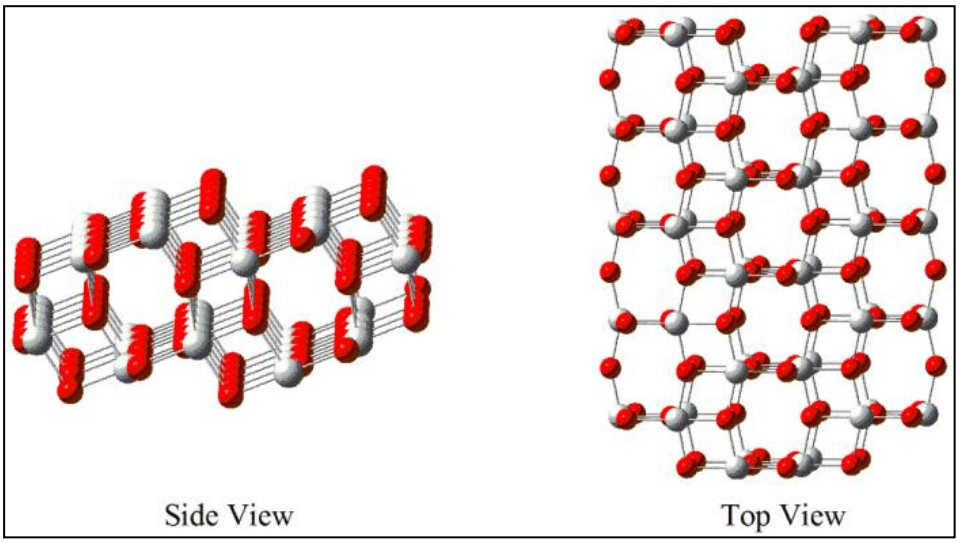

Figure S1. Initial structure of the $(TiO_2)_{48}$ cluster in side and top view.

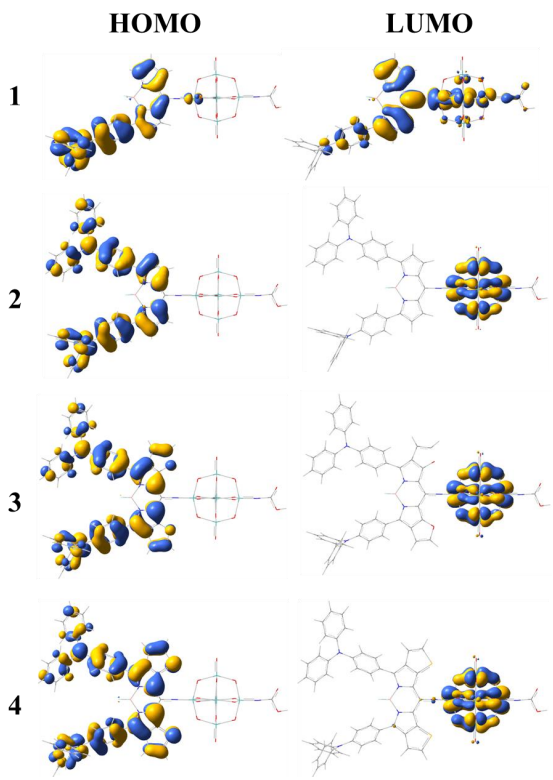

Figure S2. Frontier molecular orbital distributions of studied dyes.

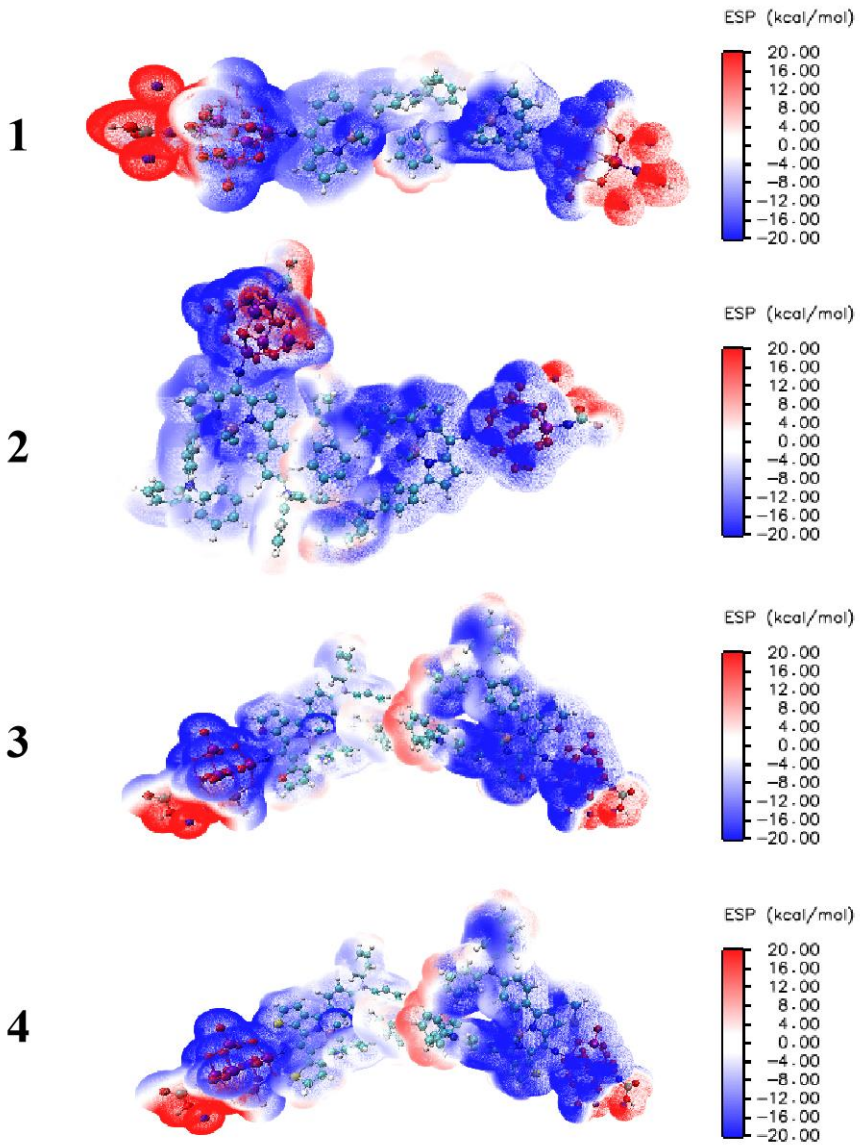

Figure S3. Electrostatic potential maps for dimers of studied dyes.

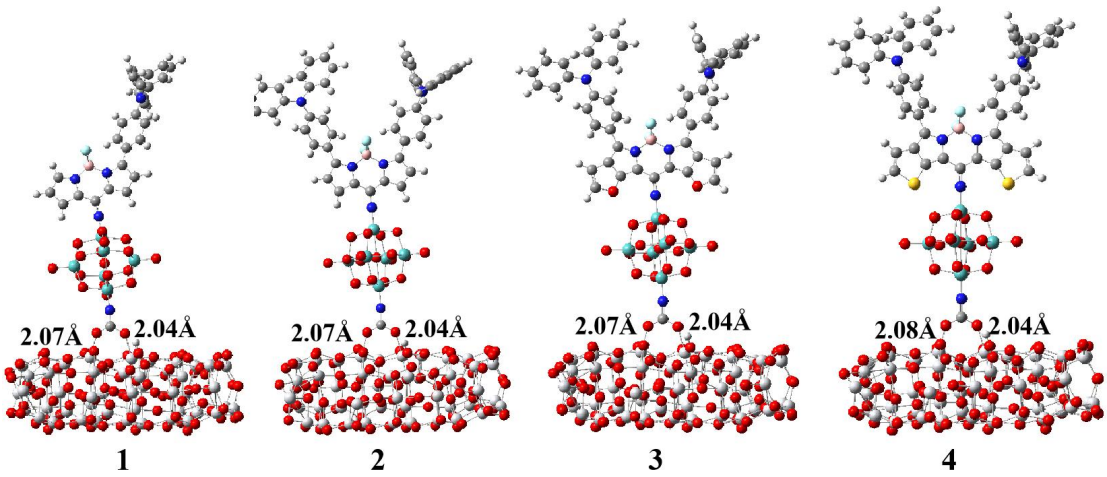

Figure S4. Optimized geometrical structures of dyes adsorbed on TiO_2.

Table S1. The calculated excitation energies E_v (eV), maximum absorption wavelengths λ_{max} (nm), oscillator strengths f and major electronic compositions of studied dyes.

dye	E_v	λ_{max}	f	Major electronic compositions
1	1.99	623	0.99	H→L(84%)
	2.86	434	0.40	H–1→L(71%)
2	1.76	703	0.55	H→L(88%)
	2.39	519	1.34	H–1→L(85%)
3	1.66	746	0.54	H→L(91%)
	2.48	501	1.47	H–1→L(81%)
4	1.58	786	0.51	H→L(91%)
	2.44	508	1.26	H–1→L(79%)