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Supporting Information

POM-based dyes featured rigidified bithiophene π linkers: Potential high-

efficient dyes for dye-sensitized solar cells

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1. Theoretical background

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

$$\eta = FF \frac{V_{\rm OC} J_{\rm SC}}{I_{\rm S}} \tag{1}$$

where J_{SC} is the short-circuit photocurrent density, V_{OC} is the open-circuit photovoltage, I_S is the intensity of the incident light and *FF* is the fill factor of the cell. Accordingly, improving J_{SC} and V_{OC} is an effective method to enhance η . The J_{SC} can be defined as follows [2]:

$$J_{\rm SC} = \int LHE(\lambda) \Phi_{\rm inject} \eta_{\rm collect} I_{\rm S}(\lambda) d\lambda$$
⁽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} . Φ_{inj} is the electron injection efficiency, and closely connected with k_{inj} , which can be described as follows:

$$k_{\rm inj} = \frac{2\pi}{h} V_{\rm DA}^2 \left(\frac{\pi}{\chi K_{\rm B} T}\right)^{1/2} \exp\left[-\frac{\Delta G_{\rm inj} + \chi}{4\chi K_{\rm B} T}\right]$$
(3)

where V_{DA} is the coupling between the donor and acceptor states and χ is the reorganization energy. ΔG_{inj} , the driving force of electron injection from excited state of dyes to TiO₂ surface, and can be determined by the following equation [3]:

$$\Delta G_{\rm inj} = E_{\rm dye}^* - E_{\rm CB} \tag{4}$$

where E_{dye}^* is the oxidation potential of dye in excited state, which is related to the oxidation potential of dye in 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 TiO₂ conduction band (CB) and experimental value -4.00 eV (vs vacuum) is used [4]. $\eta_{collect}$ is the charge

collection efficiency, which is assumed to be a constant for the same DSSCs.

As for V_{OC} , it can be defined by [5]:

$$V_{\rm OC} = \frac{E_{\rm CB}}{q} + \frac{kT}{q} \ln(\frac{n_{\rm c}}{N_{\rm CB}}) - \frac{E_{\rm redox}}{q}$$
(5)

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 and E_{redox} is the oxidation potential of electrolyte. The dye absorbed on TiO₂ surface can lead to ΔE_{CB} and further the larger E_{CB} . Hence, a dye with large n_c and ΔE_{CB} will induce a significant increase of V_{OC} .

2. Intramolecular charge transfer (ICT)

In order to evaluate the CT abilities of dyes, the CT parameters including the amount of transferred charges (q^{CT}) and corresponding effective distance (d^{CT}) were calculated [6,7]. The difference of electronic densities related to the electronic transition is given by:

$$\Delta \rho(r) = \rho_{\rm ES}(r) - \rho_{\rm GS}(r) \tag{6}$$

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

$$q^{\rm CT} = \int \rho^+(r) \,\mathrm{d}r \tag{7}$$

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

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

$$r^{-} = (x^{-}, y^{-}, z^{-}) = 1/q^{CT} \int r \rho^{-}(r) dr$$
(9)

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

3. Interaction energy (ΔE_{tot})

To elucidate the intrinsic reasons of different interaction energy (ΔE_{tot}) for the dimers of dyes, simple energy decomposition was performed. ΔE_{tot} can be decomposed as [8]:

$$\Delta E_{\text{tot}} = (\Delta E_{\text{els}} + \Delta E_{\text{ex}}) + \Delta E_{\text{orb}} = \Delta E_{\text{steric}} + \Delta E_{\text{orb}}$$
(10)

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} in above formula is orbital interaction term, which arises from the mix of occupied 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:

$$\Delta E_{\rm orb} = E_{\rm SCF, \, last} - E_{\rm SCF, \, 1st} \tag{11}$$

Note that $E_{SCF, last} = E^{complex}$, obviously we can write out the following relationship:

$$\Delta E_{\text{steric}} = \Delta E_{\text{els}} + \Delta E_{\text{ex}} = \Delta E_{\text{tot}} - \Delta E_{\text{orb}}$$
(12)

4. 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:

$$\varphi(t) = \sum_{i,j} B_{i,j}(t) \phi_{i,j} \tag{13}$$

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 be computed according to the following equation:

$$B_{i,j}(t) = \sum_{k} Q_{i,j}^{k} C_{k} exp(-\frac{i}{h} E_{k} t)$$
(14)

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

$$\varphi(0) = \sum_{k} C_k \phi(k) \tag{15}$$

The coefficient $Q_{i,j}^k$ in this equation is defined according to the expansion of $\phi(k)$ as a linear combination of the atomic orbitals:

$$\phi(k) = \sum_{j} Q_{j}^{k} \phi_{j} \tag{16}$$

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

$$HQ^{k} = E_{k}SQ^{k} \tag{17}$$

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:

$$H_{j,m} = KS_{jm} \frac{H_{jj} + H_{mm}}{2}$$
(18)

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

$$S_{jm} = \langle \varphi_j | \varphi_m \rangle \tag{19}$$

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

$$\rho_{MOL}(t) = \left|\sum_{j}^{MOL} \sum_{m} B_{j}^{*}(t) B_{m}(t) S_{jm}\right|$$
(20)

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 adsorbed dye molecular.

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D5	$\lambda_{ m max}$	f
Exp.	476	
	300	
M062X	475	0.52
	295	0.44
M06	582	0.37
	335	0.45
PBE0	595	0.35
	334	0.44
CAM-B3LYP	468	0.55
	292	0.29

 Table S1. The experimental and theoretical absorption spectra of D5.

dye	r_1	r_2	$\boldsymbol{\varTheta}_1$	Θ_2	Θ_3
1	1.462	1.419	-37.33	-7.25	0.01
2	1.348	1.423	-22.28	-2.07	-2.31
3	1.333	1.421	30.89	-1.17	-0.19
4	1.330	1.416	6.76	-0.08	0.21
5	1.331	1417	9.83	-0.11	-0.03

Table S2. Selected bond lengths r (unit in Å) and dihedral angles Θ (unit in °) of studied dyes.

Table S3. The calculated excitation energies E_v (eV), maximum absorption wavelengths λ_{max} (nm), oscillator strengths f and major electronic compositions of studied dyes.

dye	$E_{\rm V}$	$\lambda_{ m max}$	f	Major electronic compositions
1	2.61	475	0.52	H→L (85%)
2	2.47	503	0.99	H−1→L (77%)
3	2.43	511	2.55	H−1→L (85%)
4	2.30	539	1.99	H−1→L (65%)
5	2.35	528	2.52	H−1→L (76%)



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



Figure S2. Frontier molecular orbital energy levels of studied dyes.



Figure S3. Frontier molecular orbital distributions of studied dyes.



Figure S4. The key ICT parameters of studied dyes.



Figure S5. Optimized dimer structures as well as the interaction energies ΔE_{tot} for studied dyes.



Figure S6. Molecular orbital compositions of LUMOs for studied dyes.



Figure S7. The evolution of the electronic isosurfaces from 0 fs (top) to 20 fs (bottom).

Cartesian coordinate of the initial structure for $(TiO_2)_{48}$ cluster:

0	5.66400000	16.99200000	-21.74190000
0	1.88800000	15.10400000	-9.88440000
0	5.66400000	15.10400000	-9.88440000
0	3.77600000	15.10400000	-11.45910000
0	3.77600000	13.21600000	-9.08760000
0	3.77600000	16.99200000	-9.08760000
Ti	3.77600000	15.10400000	-9.48600000
0	5.66400000	16.99200000	-12.25590000
Ti	1.88800000	16.99200000	-14.22900000
0	1.88800000	16.99200000	-12.25590000
Ti	5.66400000	16.99200000	-14.22900000
Ti	3.77600000	16.99200000	-16.60050000
0	3.77600000	16.99200000	-18.57360000
Ti	7.55200000	16.99200000	-16.60050000
0	7.55200000	16.99200000	-18.57360000
0	5.66400000	15.10400000	-19.37040000
0	5.66400000	3.77600000	-19.37040000
0	3.77600000	3.77600000	-20.94510000
0	5.66400000	7.55200000	-19.37040000
0	3.77600000	7.55200000	-20.94510000
0	5.66400000	9.44000000	-21.74190000

Ο	5.66400000	11.32800000	-19.37040000
0	3.77600000	11.32800000	-20.94510000
0	5.66400000	13.21600000	-21.74190000
Ti	5.66400000	11.32800000	-21.34350000
0	7.55200000	11.32800000	-20.94510000
0	7.55200000	15.10400000	-20.94510000
Ti	5.66400000	15.10400000	-21.34350000
0	7.55200000	3.77600000	-20.94510000
0	5.66400000	5.66400000	-21.74190000
Ti	5.66400000	3.77600000	-21.34350000
Ti	5.66400000	7.55200000	-21.34350000
0	7.55200000	7.55200000	-20.94510000
0	1.88800000	3.77600000	-9.88440000
0	5.66400000	3.77600000	-9.88440000
0	3.77600000	3.77600000	-11.45910000
0	3.77600000	5.66400000	-9.08760000
Ti	3.77600000	3.77600000	-9.48600000
0	1.88800000	13.21600000	-16.20210000
0	3.77600000	13.21600000	-14.62740000
Ti	3.77600000	13.21600000	-16.60050000
0	3.77600000	11.32800000	-16.99890000
0	3.77600000	13.21600000	-18.57360000

0	5.66400000	13.21600000	-16.20210000
0	1.88800000	16.99200000	-16.20210000
0	3.77600000	16.99200000	-14.62740000
0	3.77600000	15.10400000	-16.99890000
0	5.66400000	16.99200000	-16.20210000
0	7.55200000	15.10400000	-16.99890000
0	3.77600000	9.44000000	-18.57360000
0	7.55200000	13.21600000	-18.57360000
Ti	3.77600000	11.32800000	-18.97200000
Ti	7.55200000	15.10400000	-18.97200000
Ti	1.88800000	1.88800000	-14.22900000
0	1.88800000	1.88800000	-12.25590000
0	1.88800000	1.88800000	-16.20210000
0	5.66400000	1.88800000	-12.25590000
0	3.77600000	1.88800000	-14.62740000
Ti	5.66400000	1.88800000	-14.22900000
Ti	3.77600000	1.88800000	-16.60050000
0	3.77600000	1.88800000	-18.57360000
0	5.66400000	1.88800000	-16.20210000
0	7.55200000	1.88800000	-14.62740000
Ti	7.55200000	1.88800000	-16.60050000
0	7.55200000	1.88800000	-18.57360000

0	1.88800000	5.66400000	-12.25590000
Ti	1.88800000	9.44000000	-14.22900000
Ti	1.88800000	7.55200000	-11.85750000
0	1.88800000	9.44000000	-12.25590000
0	1.88800000	7.55200000	-9.88440000
0	1.88800000	7.55200000	-13.83060000
0	1.88800000	9.44000000	-16.20210000
0	3.77600000	7.55200000	-11.45910000
0	5.66400000	9.44000000	-12.25590000
0	3.77600000	9.44000000	-14.62740000
Ti	1.88800000	13.21600000	-14.22900000
Ti	1.88800000	11.32800000	-11.85750000
0	1.88800000	13.21600000	-12.25590000
0	1.88800000	11.32800000	-9.88440000
0	1.88800000	11.32800000	-13.83060000
0	5.66400000	11.32800000	-9.88440000
0	3.77600000	11.32800000	-11.45910000
0	5.66400000	13.21600000	-12.25590000
Ti	5.66400000	13.21600000	-14.22900000
Ti	5.66400000	11.32800000	-11.85750000
0	5.66400000	11.32800000	-13.83060000
0	7.55200000	13.21600000	-14.62740000

0	7.55200000	16.99200000	-14.62740000
Ti	1.88800000	15.10400000	-11.85750000
0	1.88800000	15.10400000	-13.83060000
Ti	5.66400000	15.10400000	-11.85750000
0	5.66400000	15.10400000	-13.83060000
Ti	1.88800000	5.66400000	-14.22900000
Ti	1.88800000	3.77600000	-11.85750000
0	1.88800000	3.77600000	-13.83060000
0	1.88800000	5.66400000	-16.20210000
0	5.66400000	5.66400000	-12.25590000
0	3.77600000	5.66400000	-14.62740000
Ti	5.66400000	5.66400000	-14.22900000
Ti	3.77600000	5.66400000	-16.60050000
Ti	5.66400000	3.77600000	-11.85750000
0	3.77600000	3.77600000	-16.99890000
0	5.66400000	3.77600000	-13.83060000
0	3.77600000	5.66400000	-18.57360000
0	5.66400000	5.66400000	-16.20210000
0	7.55200000	5.66400000	-14.62740000
Ti	3.77600000	3.77600000	-18.97200000
0	7.55200000	3.77600000	-16.99890000
0	3.77600000	7.55200000	-16.99890000

0	5.66400000	7.55200000	-13.83060000
Ti	5.66400000	9.44000000	-14.22900000
Ti	3.77600000	9.44000000	-16.60050000
0	5.66400000	9.44000000	-16.20210000
0	7.55200000	9.44000000	-14.62740000
Ti	3.77600000	7.55200000	-18.97200000
Ti	7.55200000	9.44000000	-16.60050000
0	7.55200000	7.55200000	-16.99890000
0	7.55200000	9.44000000	-18.57360000
Ti	7.55200000	13.21600000	-16.60050000
0	7.55200000	11.32800000	-16.99890000
Ti	7.55200000	11.32800000	-18.97200000
Ti	7.55200000	5.66400000	-16.60050000
0	7.55200000	5.66400000	-18.57360000
Ti	7.55200000	3.77600000	-18.97200000
Ti	7.55200000	7.55200000	-18.97200000
0	3.77600000	9.44000000	-9.08760000
Ti	3.77600000	7.55200000	-9.48600000
Ti	3.77600000	11.32800000	-9.48600000
0	5.66400000	18.88000000	-19.37040000
0	3.77600000	18.88000000	-20.94510000
Ti	5.66400000	18.88000000	-21.34350000

0	7.55200000	18.88000000	-20.94510000
0	1.88800000	18.88000000	-9.88440000
0	5.66400000	18.88000000	-9.88440000
0	3.77600000	18.88000000	-11.45910000
Ti	3.77600000	18.88000000	-9.48600000
Ti	1.88800000	18.88000000	-11.85750000
0	1.88800000	18.88000000	-13.83060000
Ti	5.66400000	18.88000000	-11.85750000
0	3.77600000	18.88000000	-16.99890000
0	5.66400000	18.88000000	-13.83060000
Ti	3.77600000	18.88000000	-18.97200000
0	7.55200000	18.88000000	-16.99890000
Ti	7.55200000	18.88000000	-18.97200000