Supporting Information

Theoretical investigation on the influence of different electric field directions and strengths on the POM-based dye for dye-sensitized solar cells

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1. Theoretical background

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

$$\eta = FF\frac{\mathrm{VOCJSC}}{\mathrm{IS}} \qquad (1)$$

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:

$$J_{\mathrm{SC}} = \mathrm{e}\int_{\lambda} \mathrm{IPCE}\varphi_{\mathrm{ph.\ AM1.5G}}(\lambda)d\lambda \qquad (2)$$

where e is the unit charge, IPCE(λ) is the incident photo-to-current conversion efficiency at a fixed wavelength, $\varphi_{\mathrm{ph.\ AM1.5G}}(\lambda)$ is the corresponding photo flux of the solar radiation spectrum at a fixed wavelength.

$$\mathrm{IPCE} = LHE(\lambda)\Phi_{\mathrm{inj}}\eta_{\mathrm{reg}}\eta_{\mathrm{col}} \qquad (3)$$

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}. η_{col} is the charge collection efficiency, which is assumed to be a constant for the same DSSCs. Φ_{inj} is the electron injection efficiency, and closely connected with ΔG_{inj}, which can be determined by the following equation [2]:

$$\Delta G_{\mathrm{inj}} = E^{*}_{\mathrm{dye}} - E_{\mathrm{CB}} \qquad (4)$$

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., $E^{*}_{\mathrm{dye}} = E_{\mathrm{dye}} - E_{\mathrm{v}}$ [2]. E_{CB} is the reduction potential of the $\mathrm{TiO_2}$ conduction band (CB) and the experimental value –4.00 eV (vs vacuum) is used [3].

η_{reg} is related to the regeneration driving force ΔG_{reg}, which is defined as the difference between the redox potential of electrolyte and E_{dye} as follows [4]:

$$\Delta G_{\mathrm{reg}} = E_{\mathrm{redox}} - E_{\mathrm{dye}} \tag{5}$$

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 assesses the degree of separation between $\rho^{+}(r)$ and $\rho^{-}(r)$ based on the total densities for ground and excited states were calculated [5,6]. $\rho^{+}(r)$ and $\rho^{-}(r)$ 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:

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

$\rho_{\mathrm{ES}}(r)$ and $\rho_{\mathrm{GS}}(r)$ are proposed to represent the electronic densities of excited and ground states, respectively. And q^{CT} can be proposed:

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

The barycenters (r^{+} and r^{-}) of density distributions defined by $\rho^{+}(r)$ and $\rho^{-}(r)$ are written as the following equations:

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

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

The difference between r^{+} and r^{-} is defined as charge transfer distance, d^{CT} and t index are used to assess the degree of separation between $\rho^{+}(r)$ and $\rho^{-}(r)$ regions:

$$d^{CT} = |r^{+} - r^{-}| \tag{8}$$

$$t = d^{CT} - H \tag{9}$$

In addition, the H index is proposed as half of the sum of centroids axis along with the D–A direction.

2. Simulations of the electron injection

The time-dependent survival probabilities (TDSP) curves were defined as the probability of the photo-excited electron that 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:*

$$\varphi(t) = \sum_{i,j} B_{i,j}(t)\, \phi_{i,j} \tag{10}$$

where $\phi_{i,j}$ *represents the orbital j of the i-th atom. The expansion coefficients* $B_{i,j}(t)$ *in Eq. (7), can now be computed according to the following equation:*

$$B_{i,j}(t) = \sum_k Q^{\mathrm{k}}_{\mathrm{i,j}}\, C_k \exp(-\frac{\mathrm{i}}{\mathrm{h}} E_k t) \tag{11}$$

The coefficient C_k *in Eq. (8) is defined by the expansion of the initial state in an orthonormal basis set of* $\phi(k)$*,*

$$\varphi(0) = \sum_k C_k\, \phi(k) \tag{12}$$

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

$$\phi(k) = \sum_j Q^{\mathrm{k}}_{\mathrm{j}}\, \phi_j \tag{13}$$

The eigenvalue E_k *in Eq. (8) can be obtained by solving the extend Hückel theory (EH) eigenvalue problem:*

$$HQ^k = E_k S Q^k \tag{14}$$

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

$$H_{j,m} = KS_{jm}\frac{H_{jj} + H_{mm}}{2} \tag{15}$$

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

$$S_{jm} = <\varphi_j|\varphi_m> \tag{16}$$

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

$$\rho_{MOL}(t) = \left|\sum_j^{MOL}\sum_m B_j^*(t)B_m(t)S_{jm}\right| \tag{17}$$

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 molecule.

References

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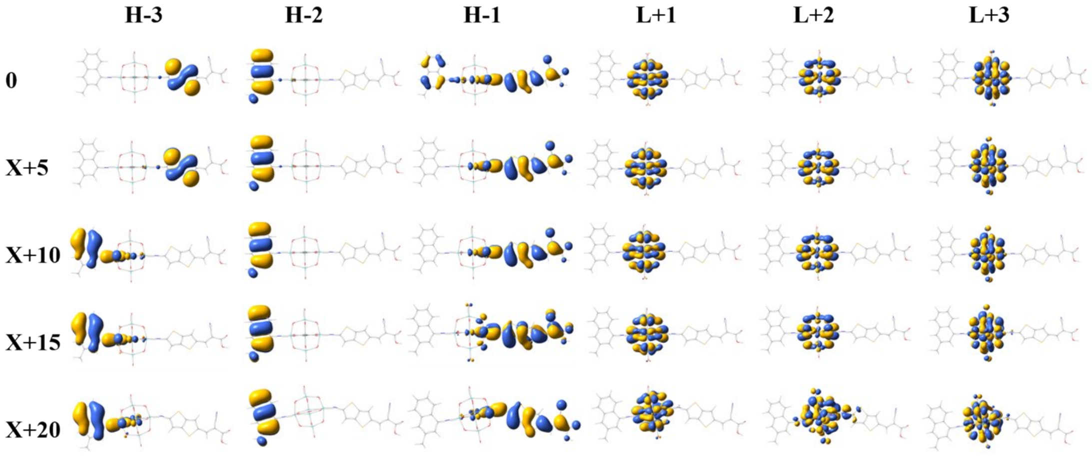

Figure S1. Orbital distributions of studied dye under different electric field strengths.

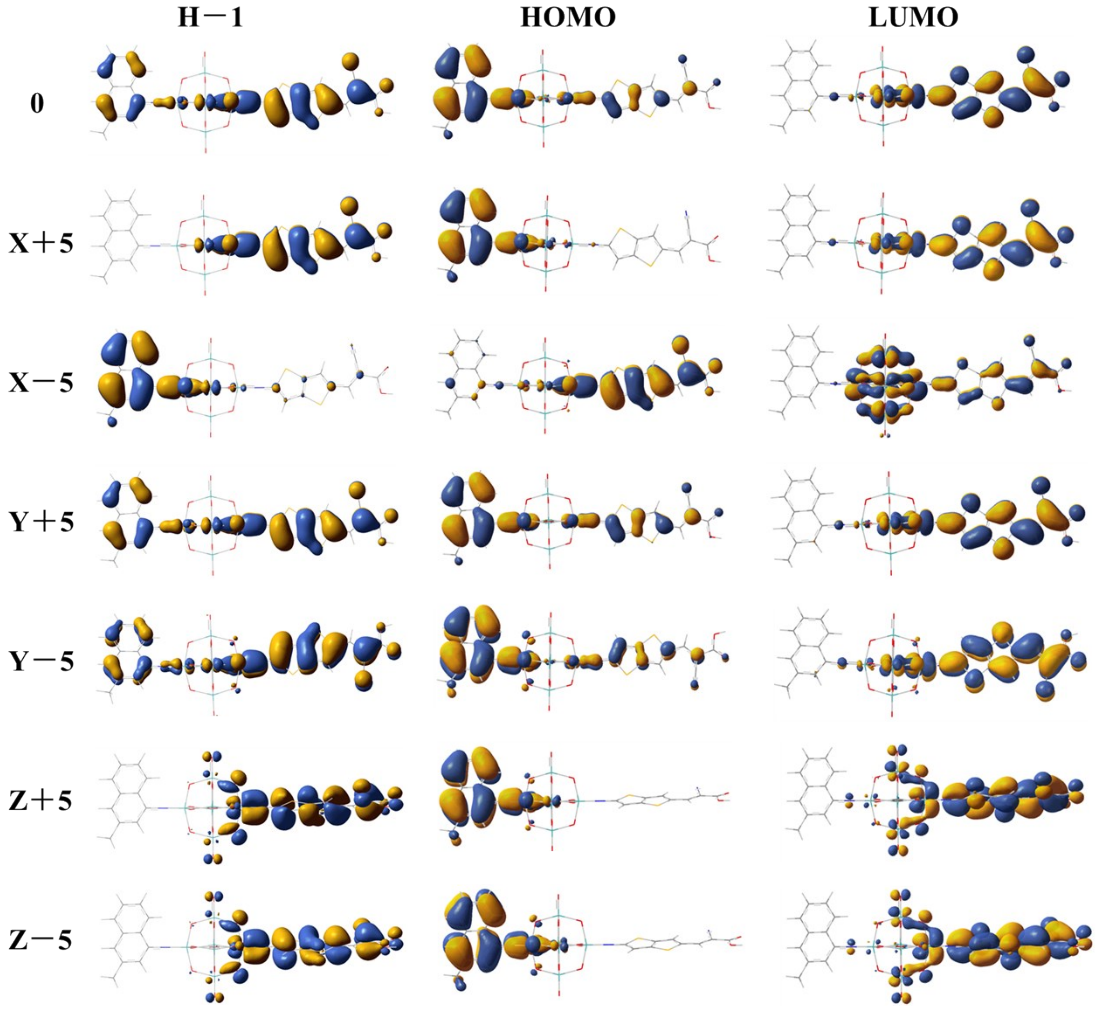

Figure S2. Frontier molecular orbital distributions of studied dye under different electric field directions.

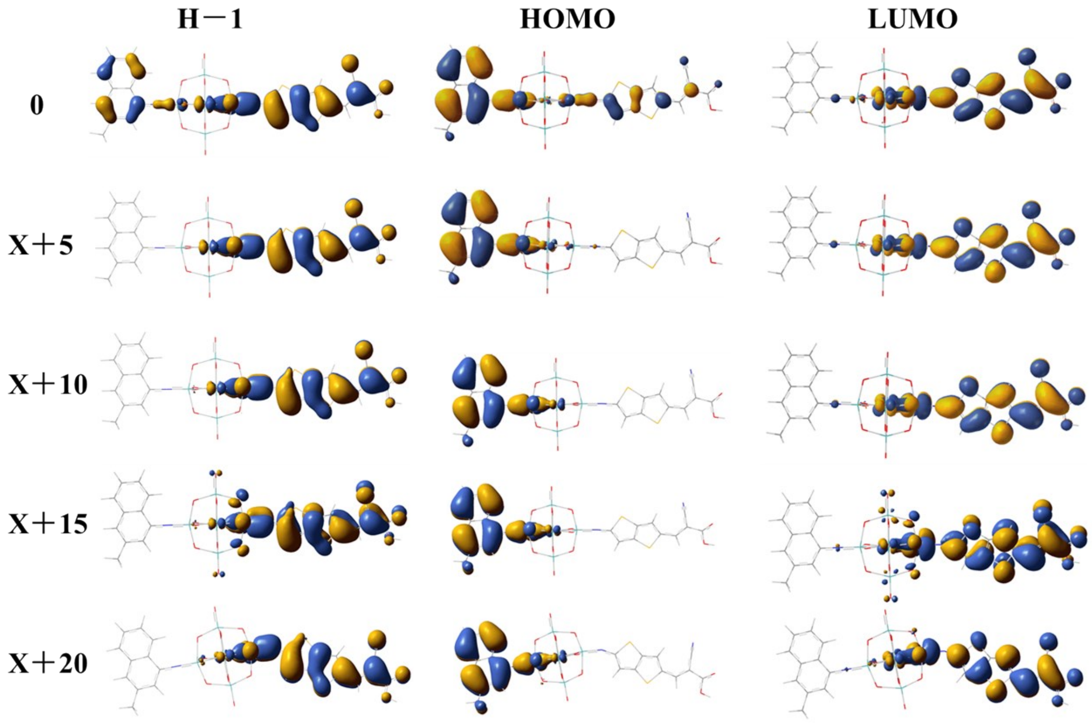

Figure S3. Frontier molecular orbital distributions of studied dye under different electric field strengths.

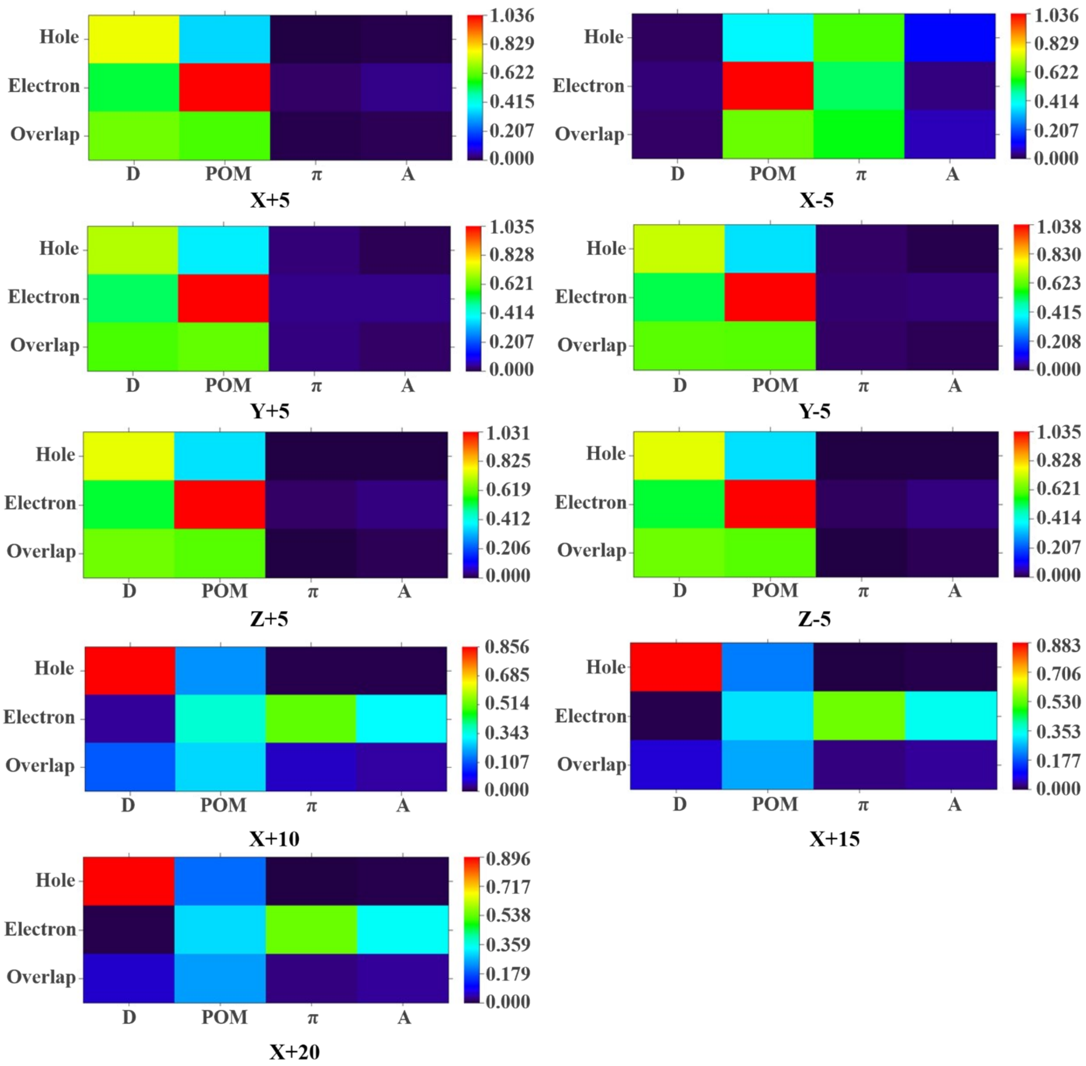

Figure S4. The heat map of studied dye under different electric field directions and strengths.

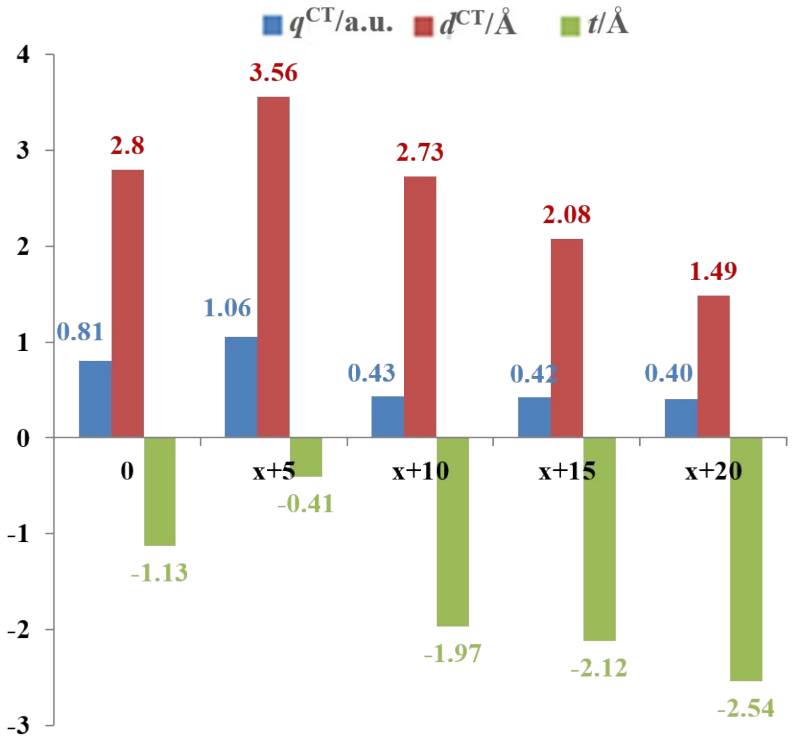

Figure S5. The key ICT parameters of studied dye under different electric field strengths.

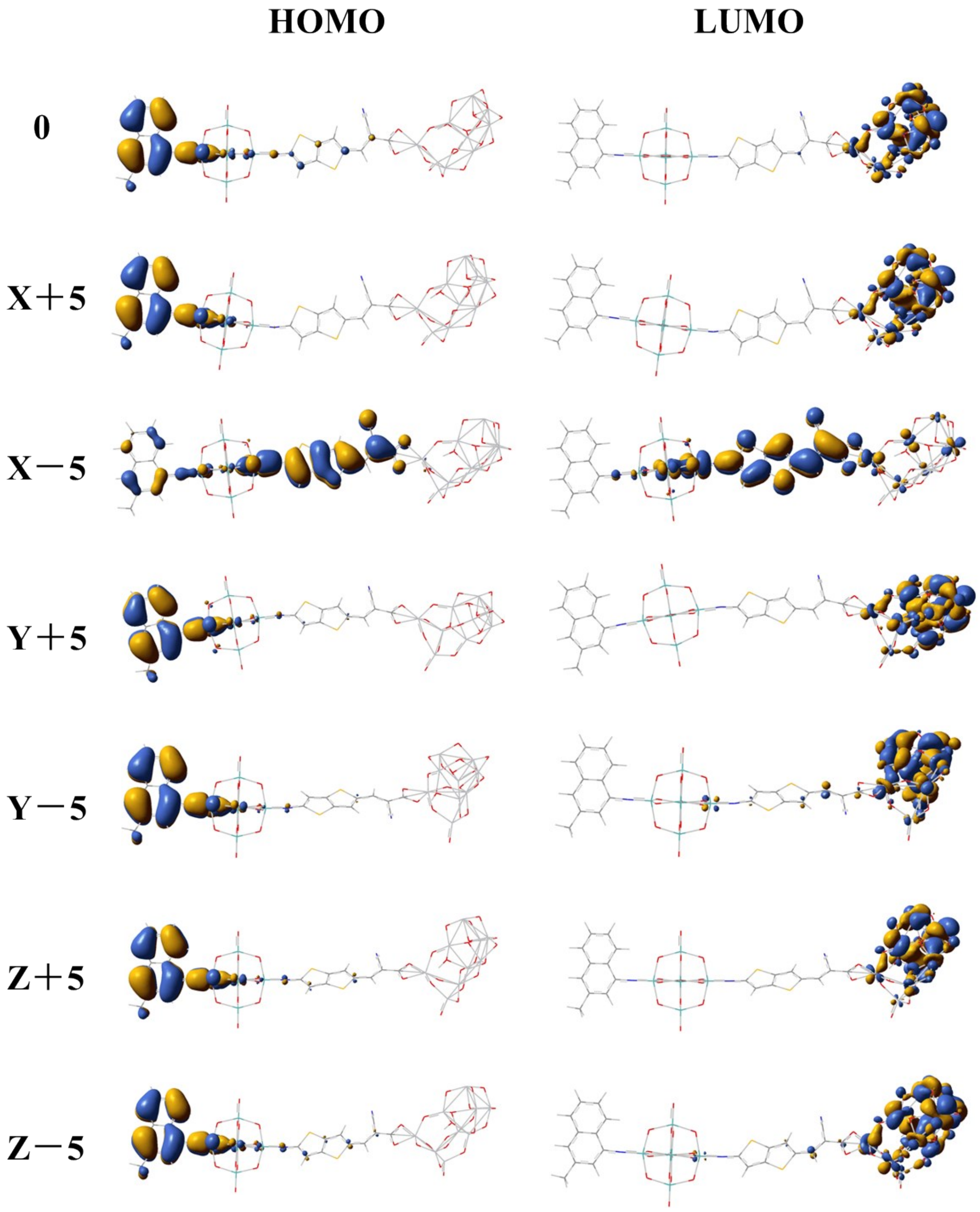

Figure S6. Frontier molecular orbital distributions of dye-TiO_2 system under different electric field directions.

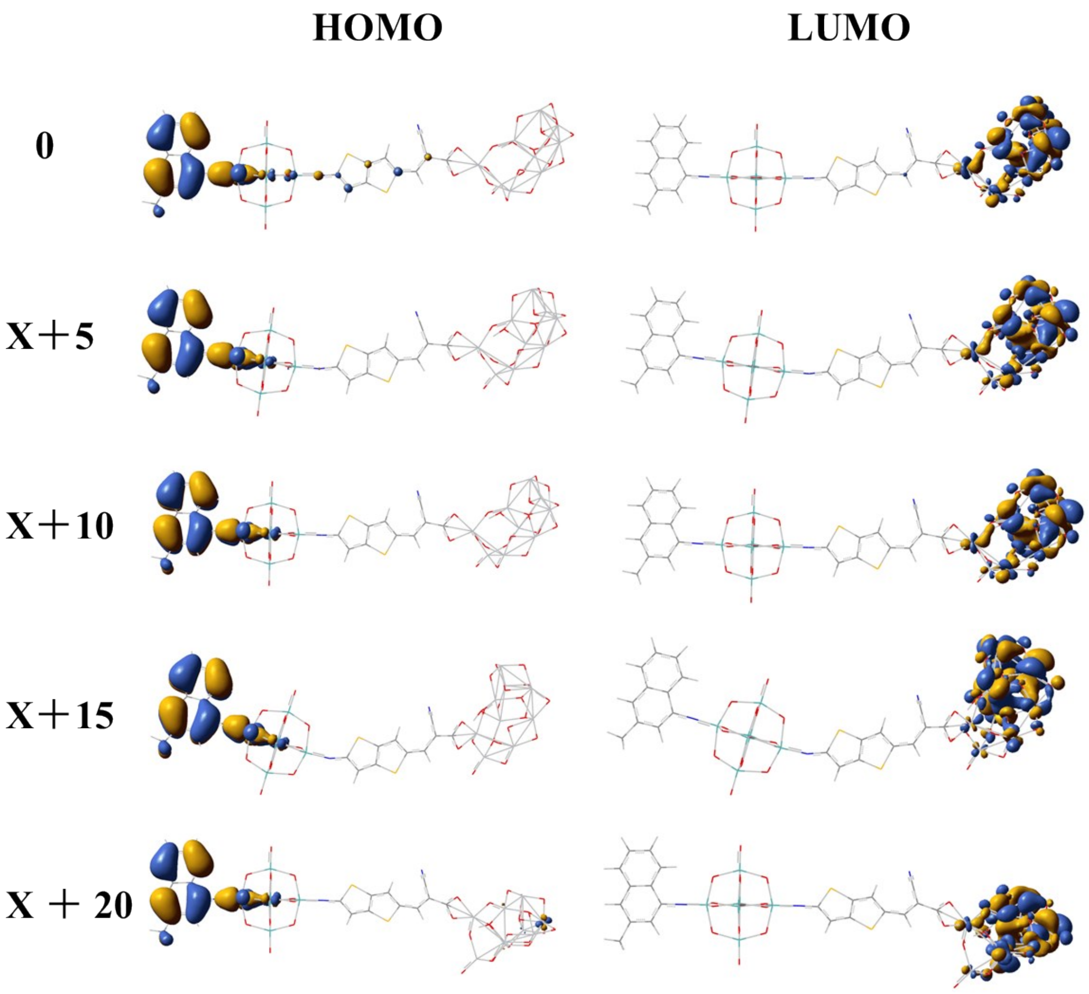

Figure S7. Frontier molecular orbital distributions of dye-TiO_2 system under different electric field strengths.

Table S1. Partial molecular orbital compositions (%) of studied dye under different electric field directions.

Field (10^{-4} a.u)	Orbital	Major component			
		D	POM	π	A
0	LUMO	0	0.30	0.31	0.32
	HOMO	0.67	0.14	0.09	0.02
X+5	LUMO	0	0.26	0.35	0.32
	HOMO	0.77	0.15	0	0
X-5	LUMO	0	0.80	0.05	0.05
	HOMO	0	0.16	0.57	0.16
Y+5	LUMO	0	0.30	0.31	0.33
	HOMO	0.61	0.11	0.14	0.02
Y-5	LUMO	0	0.29	0.34	0.29
	HOMO	0.68	0.14	0.04	0.02
Z+5	LUMO	0	0.28	0.34	0.29
	HOMO	0.79	0.15	0	0
Z-5	LUMO	0	0.28	0.34	0.29
	HOMO	0.79	0.15	0	0

Table S2. Partial molecular orbital compositions (%) of studied dye under different electric field strengths.

Field (10^{-4} a.u)	Orbital	Major assignment			
		D	POM	π	A
0	LUMO	0	0.30	0.31	0.32
	HOMO	0.67	0.14	0.09	0.02
X+5	LUMO	0	0.26	0.35	0.32
	HOMO	0.77	0.15	0	0
X+10	LUMO	0	0.24	0.29	0.37
	HOMO	0.80	0.15	0	0
X+15	LUMO	0	0.21	0.34	0.34
	HOMO	0.79	0.05	0	0
X+20	LUMO	0	0.47	0.20	0.21
	HOMO	0.80	0.05	0	0

Table S3. The calculated excitation energies E_v (eV), maximum absorption wavelengths λ_{max} (nm), oscillator strengths f and major electronic compositions of dye-TiO_2 system under different electric field directions.

Field (10^{-4} a.u)	E_v	λ_{max}	f	Major assignment
0	2.24	554	2.26	H-1→L(43%) H→L(53%)
	2.99	415	0.24	H-1→L+6(15%) H→L+15(55%)
X+5	2.21	560	2.08	H-1→L (29%) H-1→L+1(65%)
	2.90	428	0.22	H→L+13(12%) H→L+22(59%)
X-5	2.32	535	2.73	H→L(96%)
	3.09	401	0.32	H-2→L(12%) H-1→L+7(28%)
Y+5	2.25	550	2.34	H-1→L(59%) H→L(38%)
	2.90	427	0.17	H→L+13(54%)
Y-5	2.25	550	2.23	H-1→L(58%) H→L(37%)
	2.88	431	0.21	H→L+11(11%) H→L+12(59%)
Z+5	2.26	548	2.35	H-1→L(64%) H→L(28%)
	2.90	428	0.22	H→L+12(13%) H→L+13(43%)
Z-5	2.24	553	2.13	H-1→L(46%) H→L(50%)
	2.99	415	0.14	H-1→L+6(33%) H→L+17(19%)

Table S4. The calculated excitation energies E_v (eV), maximum absorption wavelengths λ_{max} (nm), oscillator strengths f and major electronic compositions of dye-TiO_2 system under different electric field strengths.

Field (10^{-4} a.u)	E_v	λ_{max}	f	Major assignment
0	2.24	554	2.26	H-1→L(43%) H→L(53%)
	2.99	415	0.24	H-1→L+6(15%) H→L+15(55%)
X+5	2.21	560	2.08	H-1→L (29%) H-1→L+1(65%)
	2.90	428	0.22	H→L+13(12%) H→L+22(59%)
X+10	2.15	576	2.07	H-1→L+2(23%) H-1→L+4(49%)
	2.80	443	0.17	H→L+23(13%) H→L+25(35%)
X+15	2.08	597	1.94	H-1→L+5(29%) H-1→L+6(48%)
	2.70	460	0.09	H→L+27(31%) H→L+29(21%)
X+20	2.05	605	0.83	H-2→L+7(19%) H-2→L+8(51%)