Supporting Information

Theoretical investigation on promising acceptor groups for POM-based dye: From electronic structure to photovoltaic conversion efficiency

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1.1 Average dye electrostatic potential (V_{EL})

The average dye electrostatic potential on TiO_2 surface was evaluated as following [1]:

$$V_{\mathrm{EL}} = \frac{1}{n_{Ti}} \sum_{i=1}^{n_{\mathrm{Ti}}} \sum_{j=1}^{n_{\mathrm{q}}} \frac{q_{\mathrm{j}}}{r_{\mathrm{ij}}} \tag{1}$$

where q_{j} is the j_{th} of the n_{q} dye point charge calculated by Merz-Kollman method [2,3] to obtain the atomic charge distributions. And r_{ij} represents the distances between these of charges and each of the titanium atoms in the superficial layer of TiO_2 cluster.

1.2 Details about dissociative (D) and molecular (M) adsorption modes

The dissociative adsorption modes **3/4-D1 to 3/4-D4** and **3/4-D5 to 3/4-D8** are in different adsorption directions. For **3/4-D1**, **3/4-D2**, **3/4-D5** and **3/4-D6** configurations, the O/O atoms coordinate with Ti_{5c} atoms and hydrogen bonds are also presented in **3/4-D2** and **3/4-D6**. The O/N atoms in **3/4-D3** and **3/4-D4** modes coordinate with Ti atoms, and the configurations of **3/4-D7** and **3/4-D8** are similar to **3/4-D3** and **3/4-D4**, with different adsorption directions. Moreover, configurations **3/4-M1** and **3/4-M2** are the corresponding molecular adsorption modes to **3/4-D1** and **3/4-D5**.

References

[1] Ronca, E., Pastore, M., Belpassi, L., Tarantelli, F., Angelis, F. D. Influence of the dye molecular structure on the TiO_2 conduction band in dye-sensitized solar cells: disentangling charge transfer and electrostatic effects. *Energy Environ. Sci.* **2013**, *6*, 183–193.

[2] Singh, U. C., Kollman, P. A. An approach to computing electrostatic charges for molecules. *J. Comput. Chem.* **1984**, *5*, 129–145.

[3] Besler, B. H., Merz, K. M., Kollman, P. A. Atomic charges derived from semiempirical methods. *J. Comput. Chem.* **1990**, *11*, 431–439.

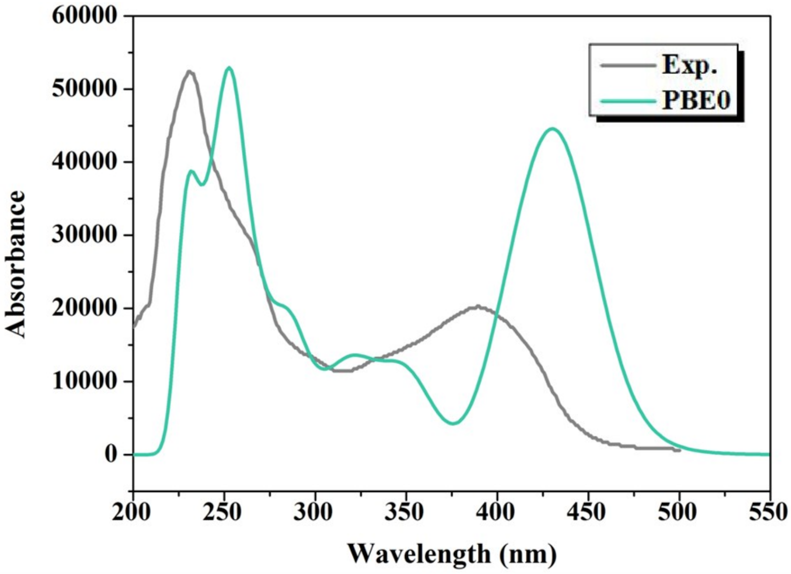


Figure S1. The experimental and theoretical absorption spectra of $[Mo_6O_{18}(N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3)]^{2-}$.

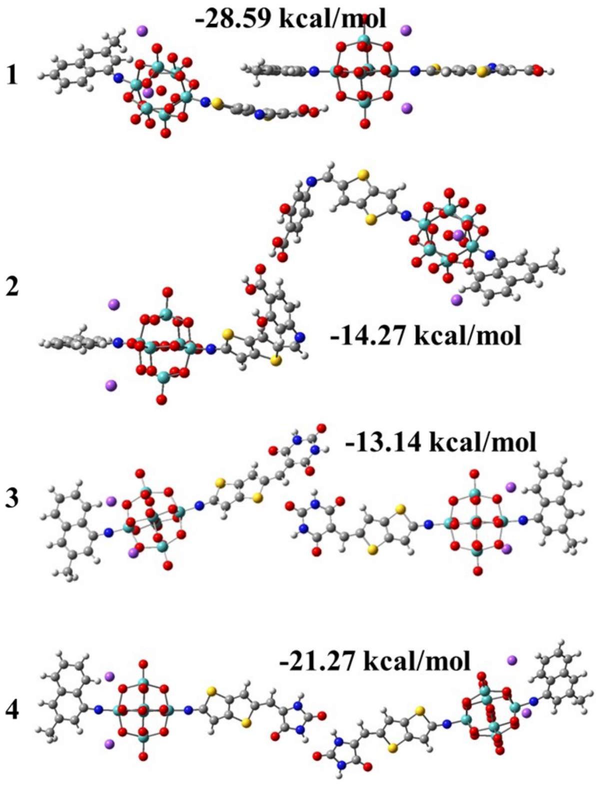
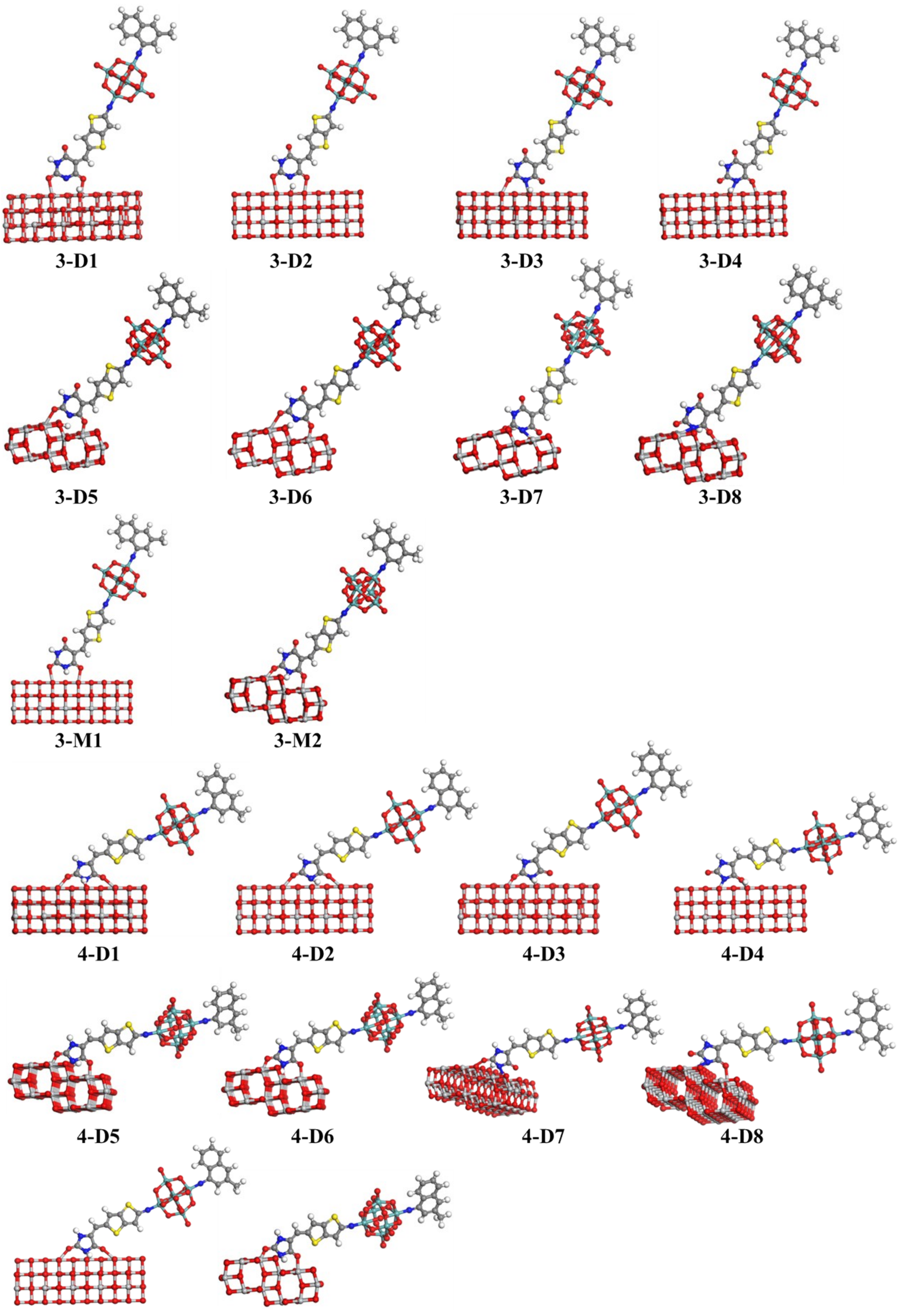


Figure S2. Optimized most stable dimer structures as well as the interaction energies ΔE_{tot} for studied dyes.



3-D1 3-D2 3-D3 3-D4

3-D5 3-D6 3-D7 3-D8

3-M1 3-M2

4-D1 4-D2 4-D3 4-D4

4-D5 4-D6 4-D7 4-D8

4-M1 4-M2

Figure S3. Possible adsorption configurations for dyes **3** and **4** on TiO_2 surface.

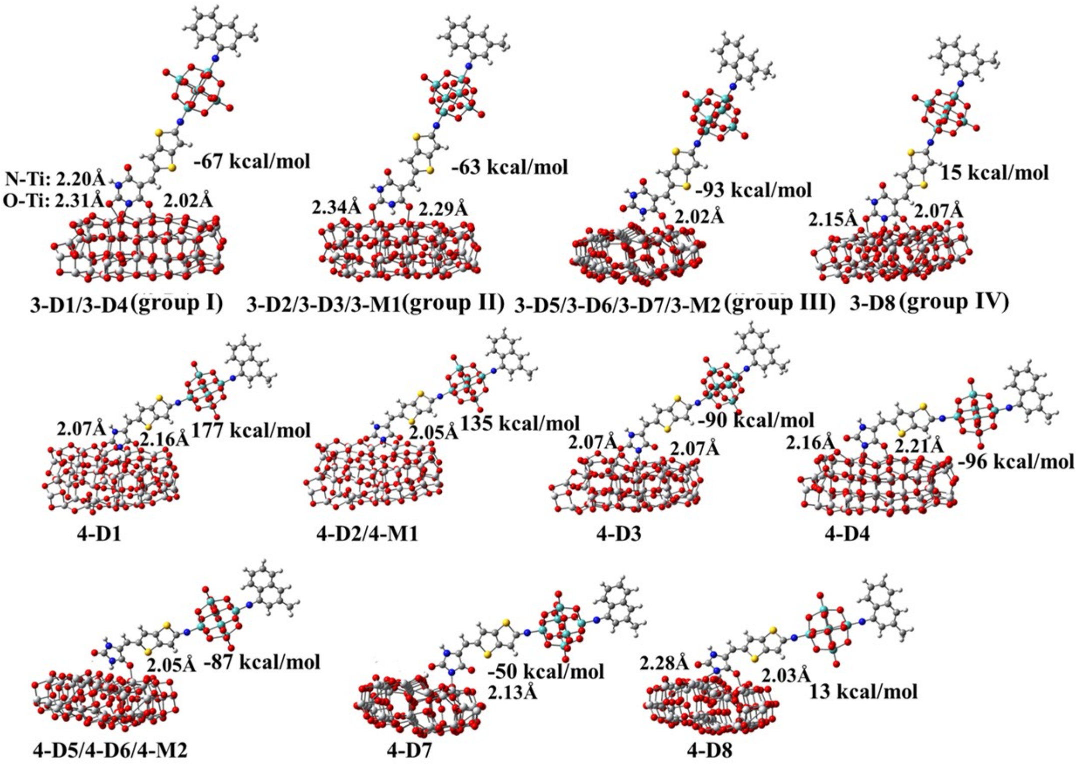


Figure S4. Optimized geometrical structures with adsorption energies (E_{ads}) and specific interatomic distances for dyes **3** and **4** on TiO_2 surface.

Table S1. The theoretical absorption spectra data of $[Mo_6O_{18}(N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3)]^{2-}$.

$[Mo_6O_{18}(N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3)]^{2-}$	λ_{max} (nm)	f
PBE0	255	0.13
	436	0.38

Table S2. The calculated excitation energies E_v (eV), maximum absorption wavelengths λ_{max} (nm), oscillator strengths f and major electronic compositions for dimers of dyes **1–4**.

dye	E_v	λ_{max}	f	Major electronic compositions
1-dimer	2.43	511	1.96	H–3→L(44%) H–1→L+3(32%)
	2.97	418	0.22	H–1→L+12(30%) H–1→L+15(36%)
2-dimer	2.62	474	2.18	H–1→L+2(12%) H→L+3(62%)
	2.95	421	0.20	H–3→L+8(57%) H–3→L+9(12%)
3-dimer	2.32	534	4.82	H–1→L+2(51%) H→L+3(40%)
	3.05	407	0.18	H–2→L+15(39%) H–2→L+17(21%)
4-dimer	2.26	549	2.93	H–1→L+2(22%) H→L+3(28%)
	2.67	465	0.20	H→L+13(47%) H→L+15(31%)