

Supporting Information

Theoretical screening promising donor and π -linker groups for POM-based Zn-porphyrin dyes in dye-sensitized solar cells

Yu Gao ^a, Wei Guan ^a, Likai Yan ^{a,*}, Yanhong Xu ^{b,*}

^a Institute of Functional Material Chemistry, National & Local United Engineering Lab for Power Battery, Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China, Fax: +86-431-5684009.

^b Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Jilin Normal University, Ministry of Education, Changchun 130103, Jilin, China.

* Corresponding author, E-mail address: yanlk924@nenu.edu.cn (L. K. Yan), xuyh@jlnu.edu.cn (Y. H. Xu).

1.1 Details about the average dye electrostatic potential (V_{EL})

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

$$V_{EL} = \frac{1}{n_{Ti}} \sum_{i=1}^{n_{Ti}} \sum_{j=1}^{n_q} \frac{q_j}{r_{ij}} \quad (1)$$

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 the number of electron transferred from dyes to TiO_2 (n_{CT})

Three terms were defined in the CDA theory based on the fragment orbitals (FO) as follows:

$$d_i = \sum_{m \in A} \sum_{n \in B}^{occ} \sum_{vir} \eta_i C_{m,i} C_{n,i} S_{m,n} \quad (2)$$

$$b_i = \sum_{m \in A} \sum_{n \in B}^{vir} \sum_{occ} \eta_i C_{m,i} C_{n,i} S_{m,n} \quad (3)$$

$$r_i = \sum_{m \in A} \sum_{n \in B}^{occ} \sum_{occ} \eta_i C_{m,i} C_{n,i} S_{m,n} \quad (4)$$

where *vir* and *occ* represent virtual and occupied orbitals, d_i is the number of electrons donated from A to B, and b_i is the electron numbers back donated from B to A; r_i is the close-shell interaction between two occupied FOs in A and B; i and η are index and occupation number of MO of complex, respectively; $S_{m,n} = \int \varphi_m(r) \varphi_n(r) dr$ is the overlap integral between FO m and FO n ; $C_{m,i}$ is the coefficient of FO m in MO i of complex; and $C_{n,i}$ is the coefficient of FO n in MO i of complex. Here FO is the fragment orbital, and MO is the molecular orbital of the fragment in its isolated state.

References

- [1] Ronca, E., Pastore, M., Belpassi, L., Tarantelli, F., Angelis, F. D. Influence of the dye molecular structure on the TiO₂ 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.

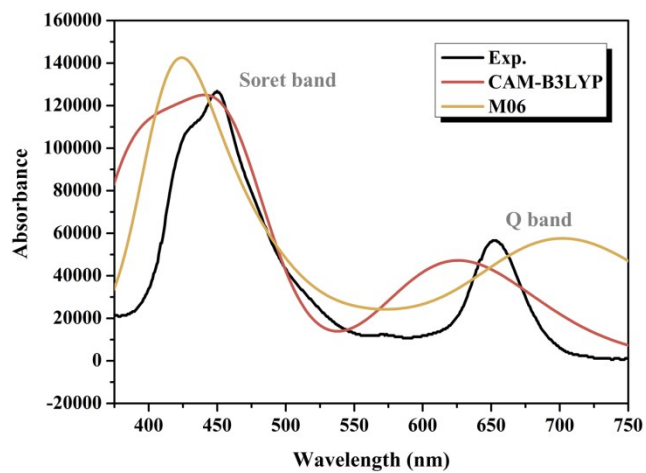


Figure S1. The experimental and theoretical absorption spectra of SM315.

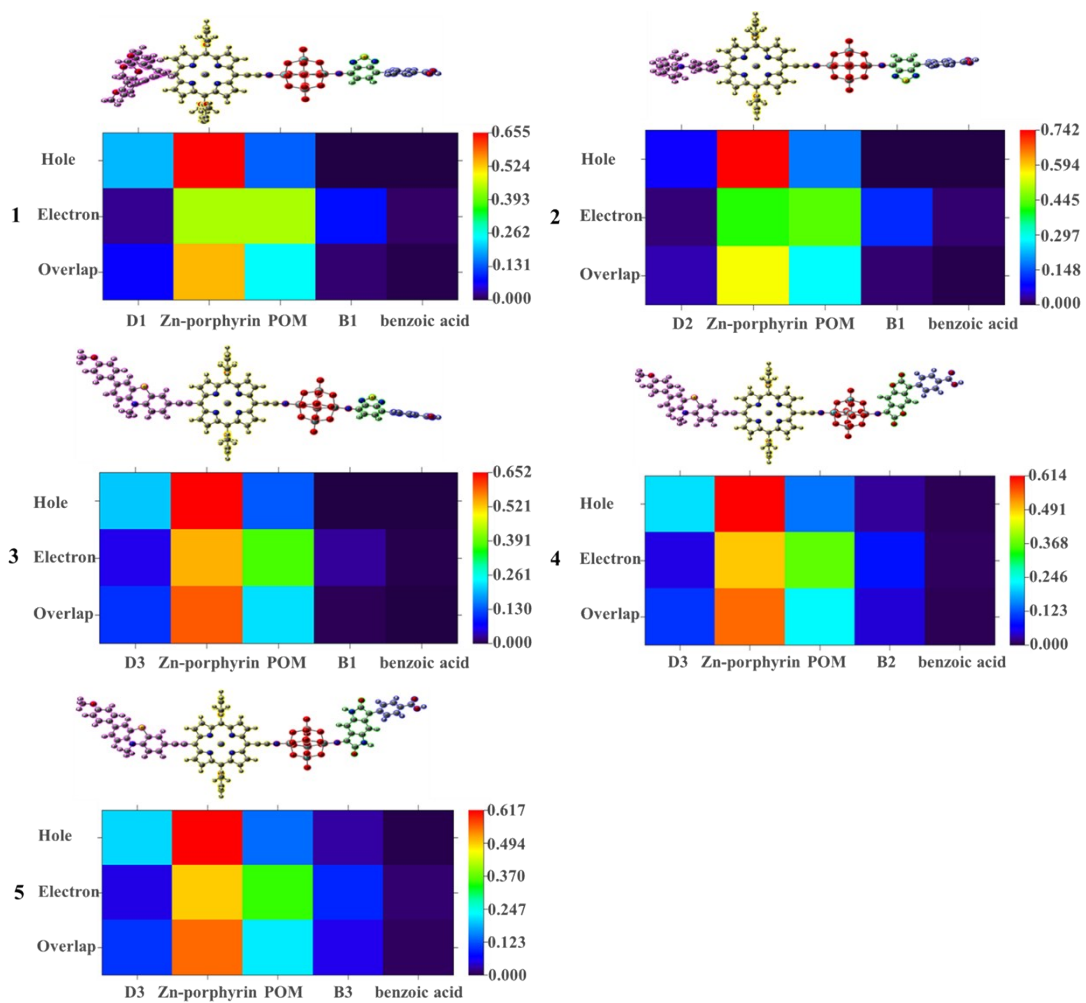


Figure S2. The heat maps of dyes 1–5.

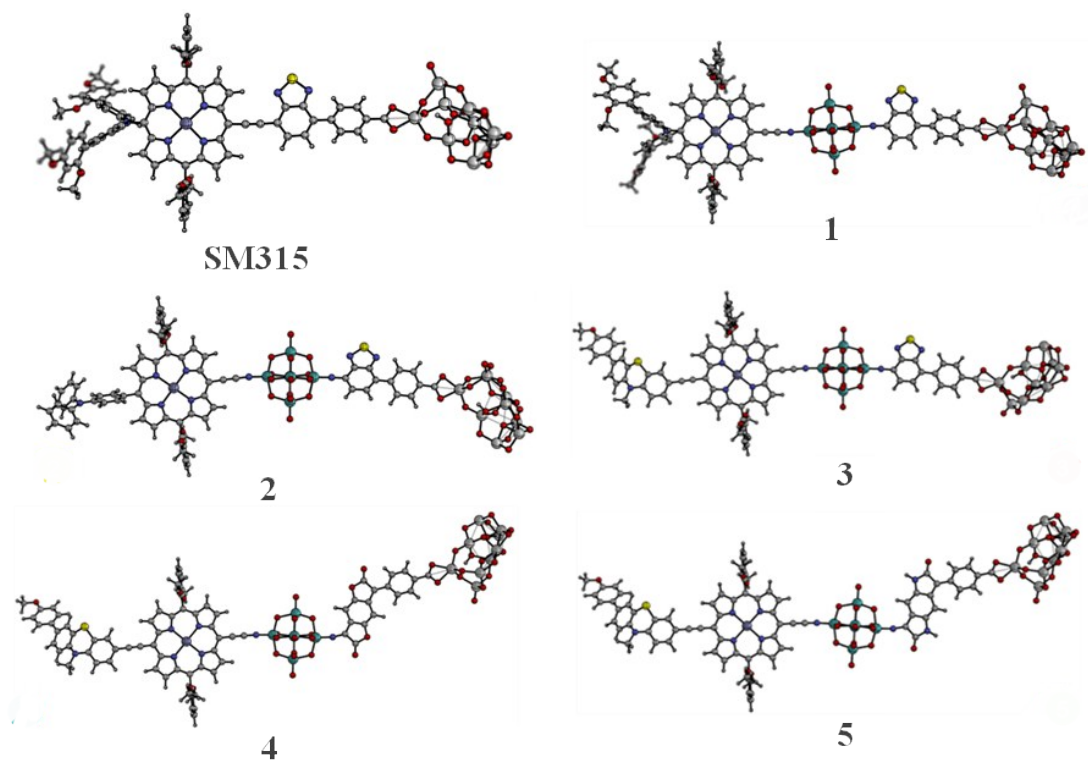


Figure S3. Optimized geometrical structure of studied dyes adsorbed onto the $(\text{TiO}_2)_9$ cluster.

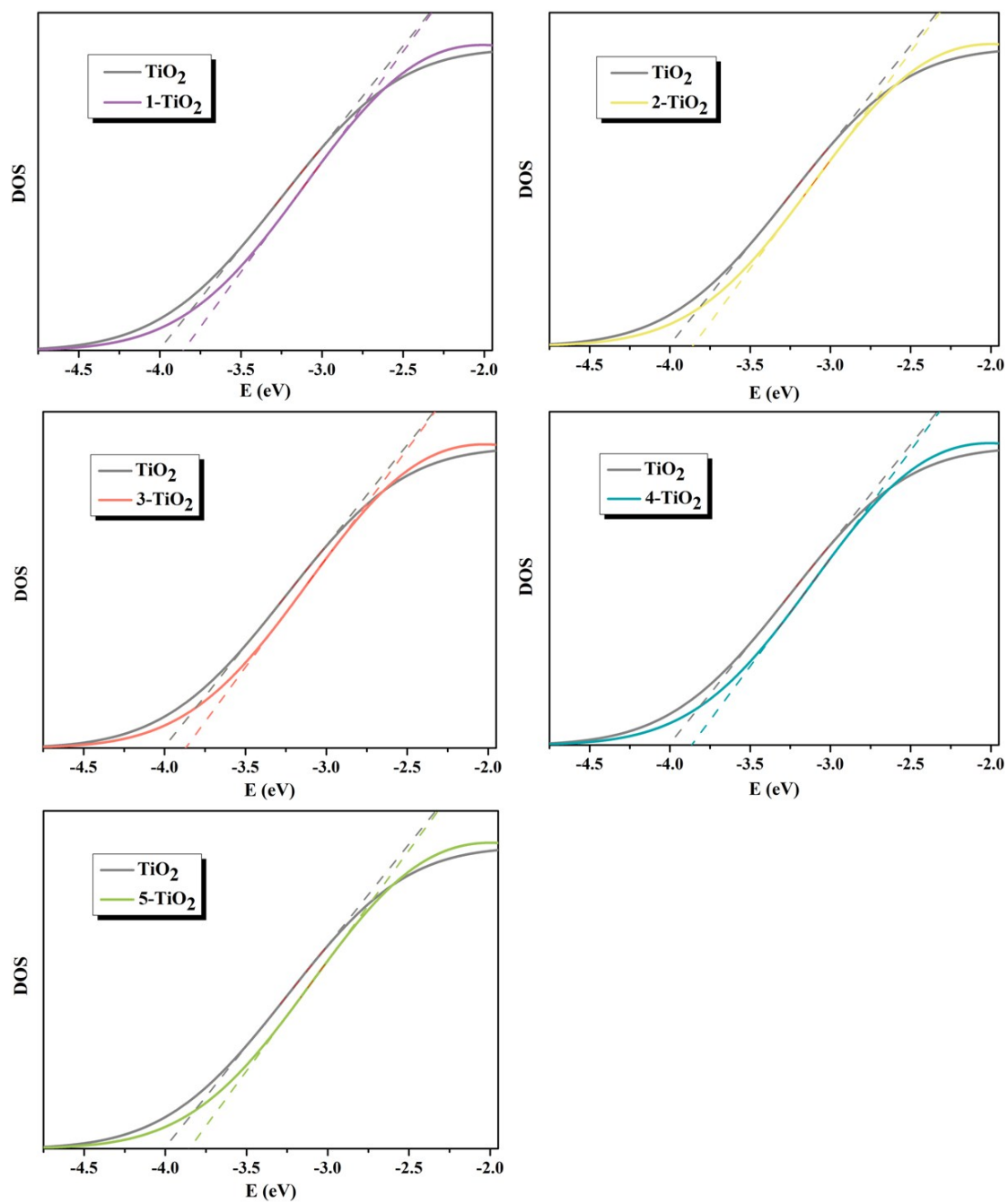


Figure S4. Total and partial density of states (DOS) of dyes-(TiO₂)₉ complexes.

Table S1. The experimental and theoretical maximum absorption wavelengths λ_{\max} (nm) and molar absorption coefficient ε .

SM315	λ_{\max}	$\varepsilon(10^3 \text{ M}^{-1} \text{ cm}^{-1})$
Exp.	454	117
	668	53
CAM-B3LYP	459	117
	626	47
M06	432	139
	706	58

Table S2. CB shift (ΔE_{CB} , eV), transfer charge (n_{CT} , e^-) for dyes absorbed onto TiO_2 and average electrostatic potential (V_{EL} , eV) of studied dyes.

dye	ΔE_{CB}	n_{CT}	V_{EL}
SM315	0.052	0.596	-0.336
1	0.151	0.646	-0.450
2	0.150	0.646	-0.450
3	0.138	0.647	-0.450
4	0.143	0.648	-0.444
5	0.155	0.655	-0.444