Supporting Information

Configuration effect in polyoxometalate-based dyes on the performance of DSSCs: An insight from theoretical perspective

Yu Gao, Wei Guan, Xue-Song Wang, Ran Jia, Li-Kai Yan*, and Zhong-Min Su

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.

*Corresponding author, E-mail address: yanlk924@nenu.edu.cn.

1. Theoretical background

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

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

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 [2]:

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

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:

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

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 TiO$_2$ surface, and can be determined by the following equation [3]:

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

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 TiO$_2$ 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]:

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

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 TiO$_2$ 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. Details about the average dye electrostatic potential (V_{EL})

The average dye electrostatic potential on the TiO$_2$ surface was evaluated by the following [6]:

$$V_{EL} = \frac{1}{nTi} \sum_{i=1}^{n_{T_i}} \sum_{j=1}^{n_q} \frac{q_j}{r_{ij}} \qquad (6)$$

where q_j is the j_{th} of the n_q dye point charge calculated by Merz-Kollman method [7,8] 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.

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:

$$\varphi(t) = \sum_{i,j} B_{i,j}(t)\, \phi_{i,j} \tag{7}$$

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

$$B_{i,j}(t) = \sum_k Q_{i,j}^k\, C_k exp(-\frac{i}{h} E_k t) \tag{8}$$

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

$$\varphi(0) = \sum_k C_k \phi(k) \tag{9}$$

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:

$$\phi(k) = \sum_j Q_j^k \phi_j \tag{10}$$

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

$$HQ^k = E_k SQ^k \tag{11}$$

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:

$$H_{j,m} = KS_{jm} \frac{H_{jj} + H_{mm}}{2} \tag{12}$$

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

$$S_{jm} = <\varphi_j | \varphi_m> \tag{13}$$

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

$$\rho_{\text{MOL}}(t) = |\sum_{j}^{MOL} \sum_{\text{m}} B_j^*(t) B_{\text{m}}(t) S_{jm}| \tag{14}$$

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.

References

[1] Grätzel, M. Recent advances in sensitized mesoscopic solar cells. Acc Chem Res 2009; 42: 1788-1798.

[2] Zhang JZ, Zhang J, Li HB, Wu Y, Xu HL, Zhang M, et al. Modulation on charge recombination and light harvesting toward high-performance benzothiadiazole-based sensitizers in dye-sensitized solar cells: A theoretical investigation. J Power Sources 2014; 267: 300-308.

[3] Katoh R, Furube A, Yoshihara T, Hara K, Fujihashi G, Takano S, et al. Efficiencies of electron injection from excited N3 dye into nanocrystalline semiconductor (ZrO_2, TiO_2, ZnO, Nb_2O_5, SnO_2, In_2O_3) films. J Phys Chem B 2004; 108: 4818-4822.

[4] Grätzel M. Photoelectrochemical cells. Nature 2001; 414: 338-344.

[5] Ning ZJ, Fu Y, Tian H. Improvement of dye-sensitized solar cells: what we know and what we need to know. Energy Environ Sci 2010; 3: 1170-1181.

[6] 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.

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

[8] Besler, B. H., Merz, K. M., Kollman, P. A. Atomic charges derived from semiempirical methods. *J. Comput. Chem.* **1990**, *11*, 431–439.
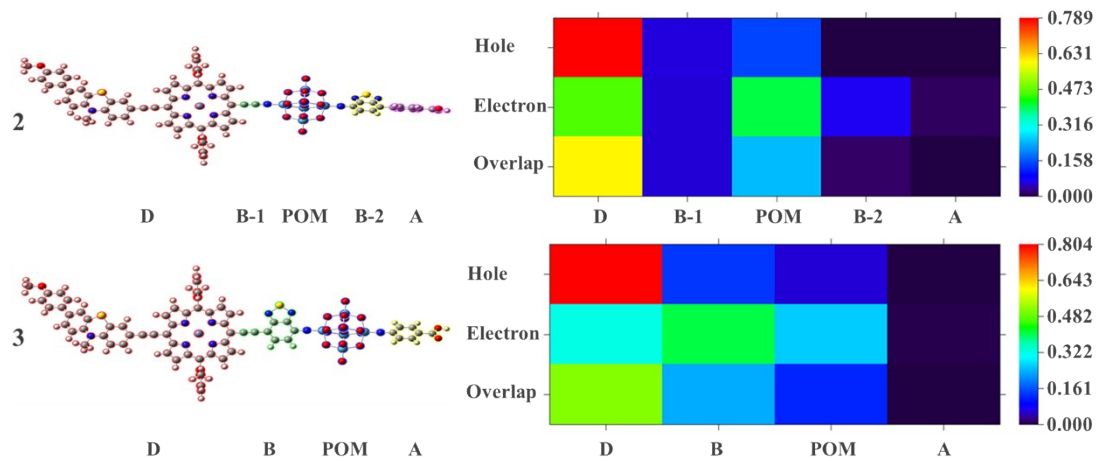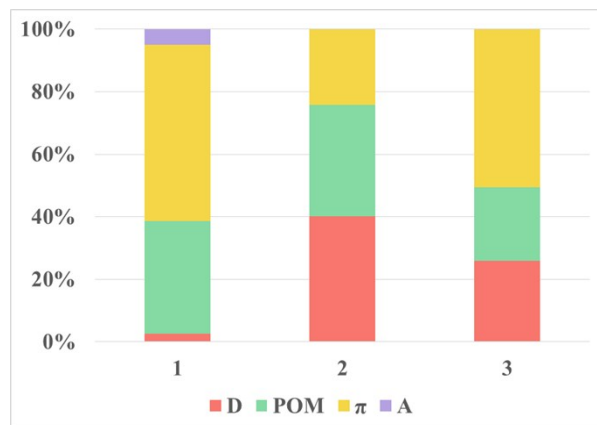
Figure S1. The heat map of dyes **2** and **3**.

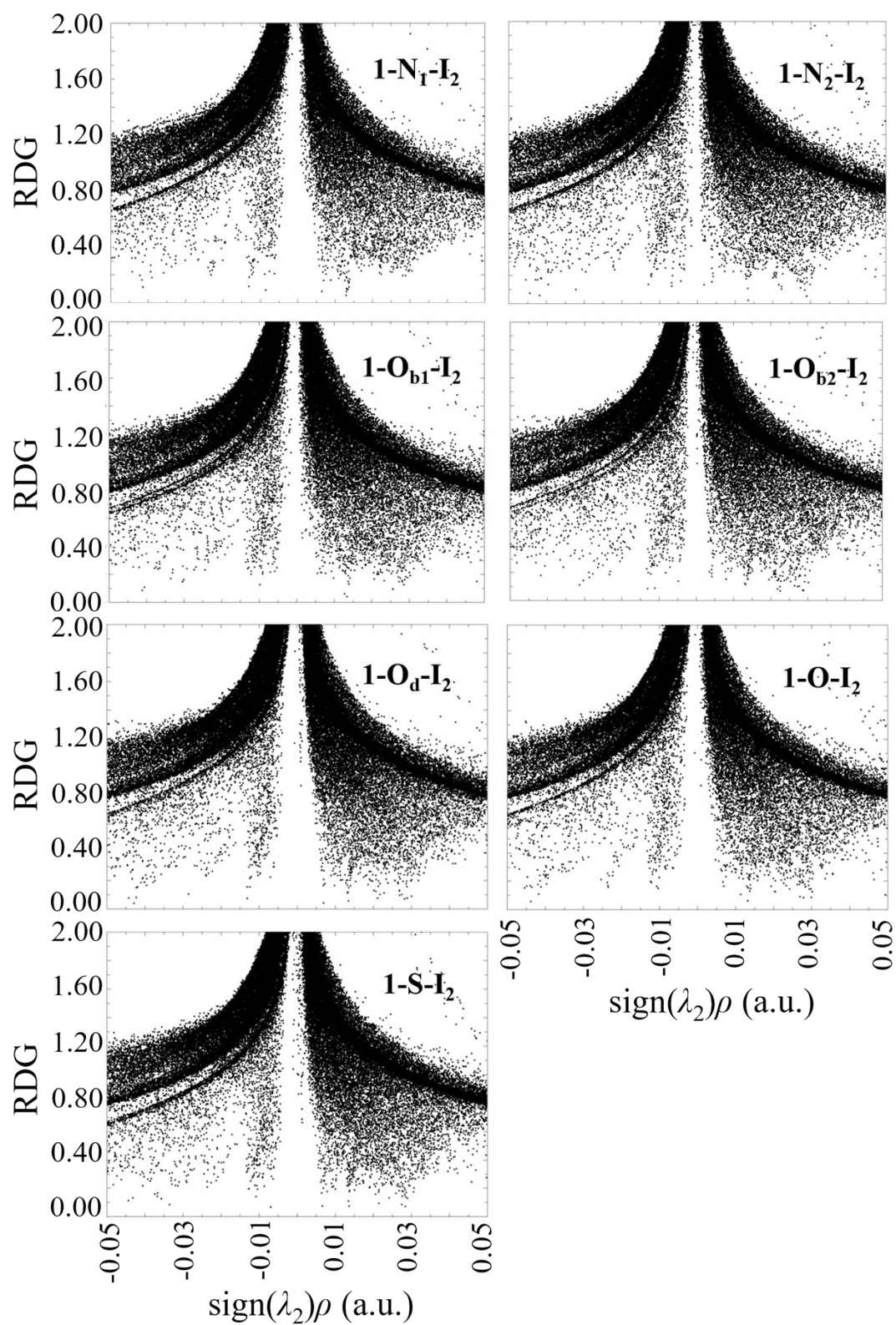**Figure S2.** Molecular orbital compositions of LUMOs for studied dyes.

Figure S3 The plots of RDG versus electron density ρ (r) multiplied by the sign of second Hessian eigenvalue λ_2 for dye **1** and I_2.
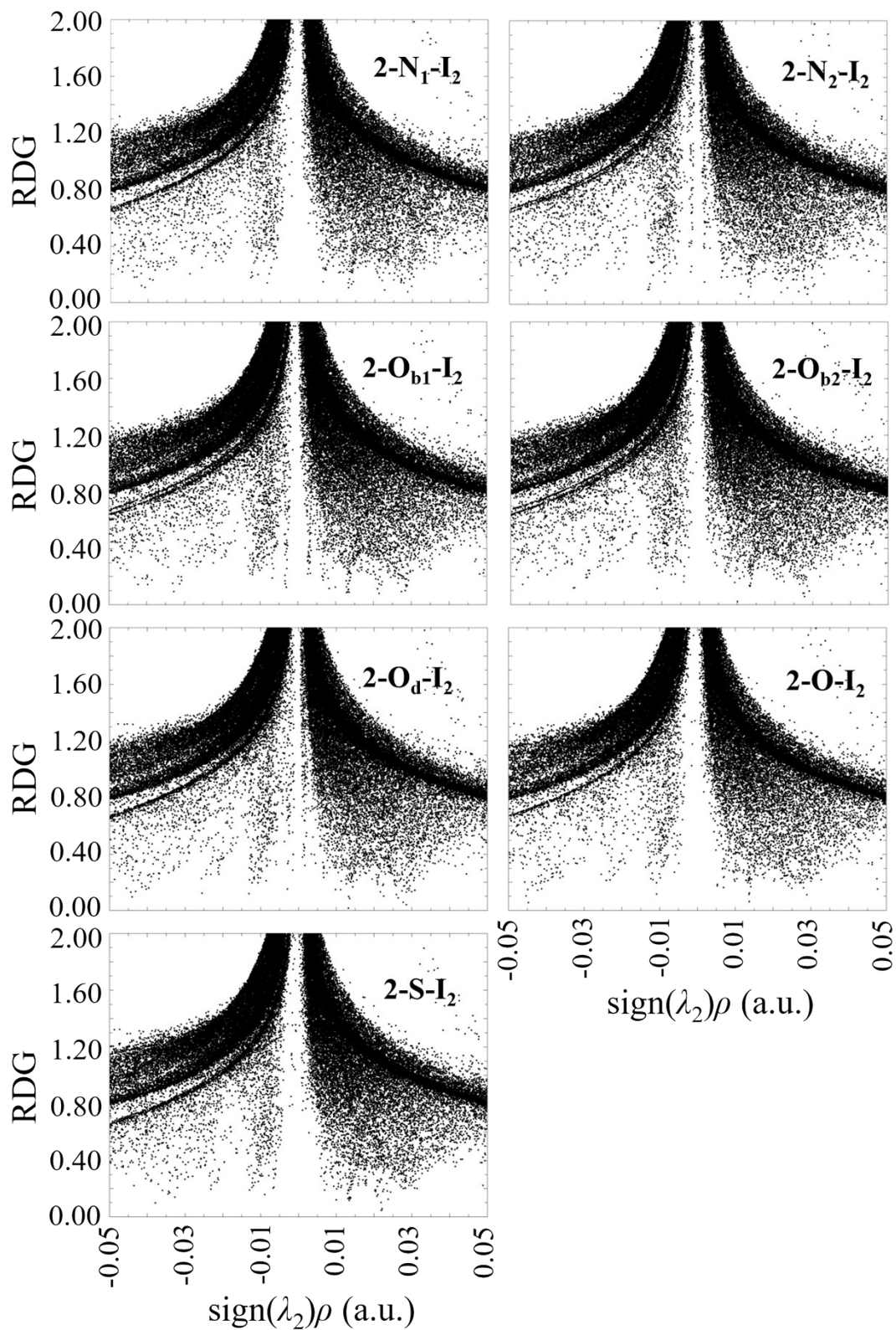
Figure S4. The plots of RDG versus electron density ρ (r) multiplied by the sign of second Hessian eigenvalue λ_2 for dye **2** and I_2.
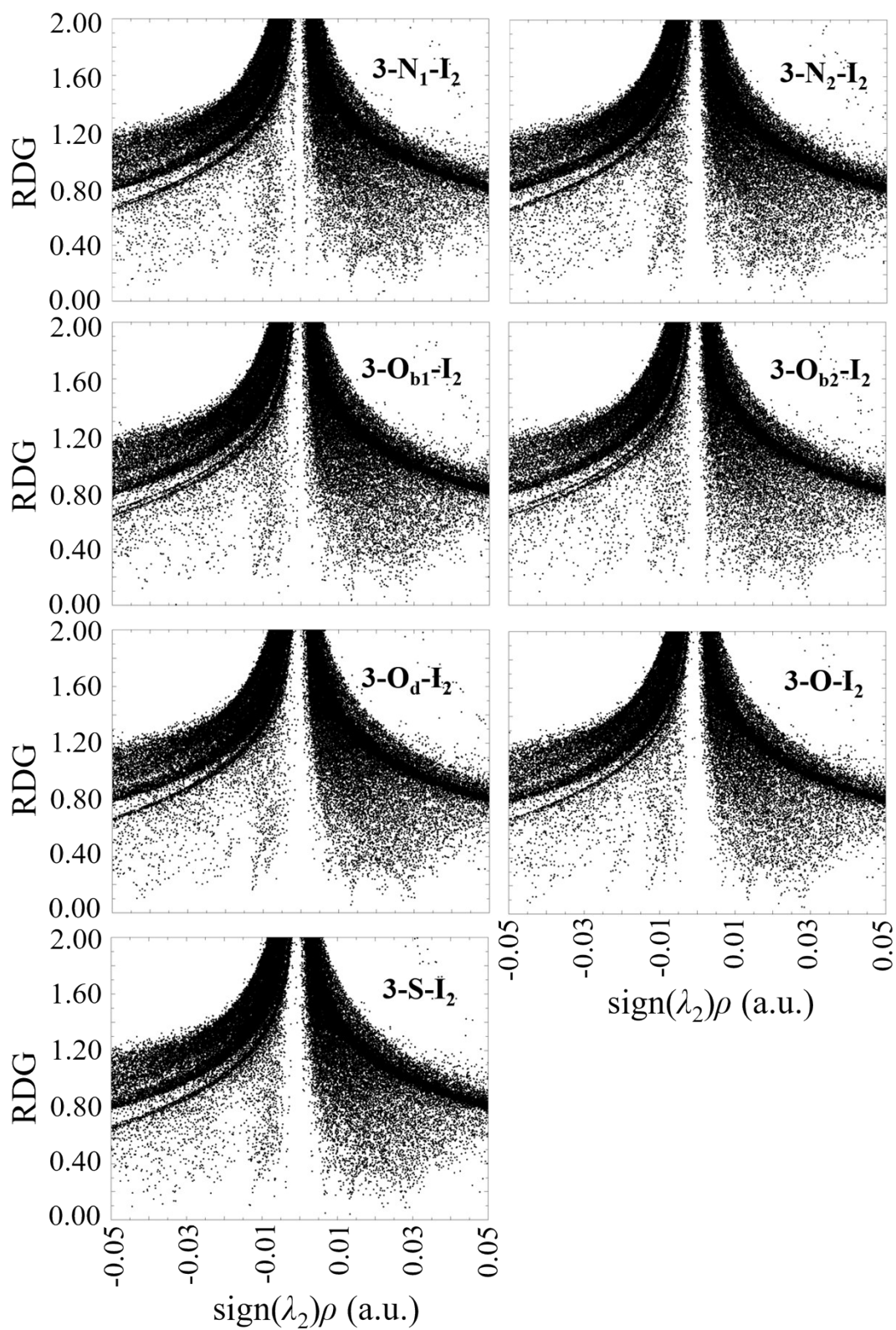
Figure S5. The plots of RDG versus electron density ρ (r) multiplied by the sign of second Hessian eigenvalue λ_2 for dye **3** and I_2.
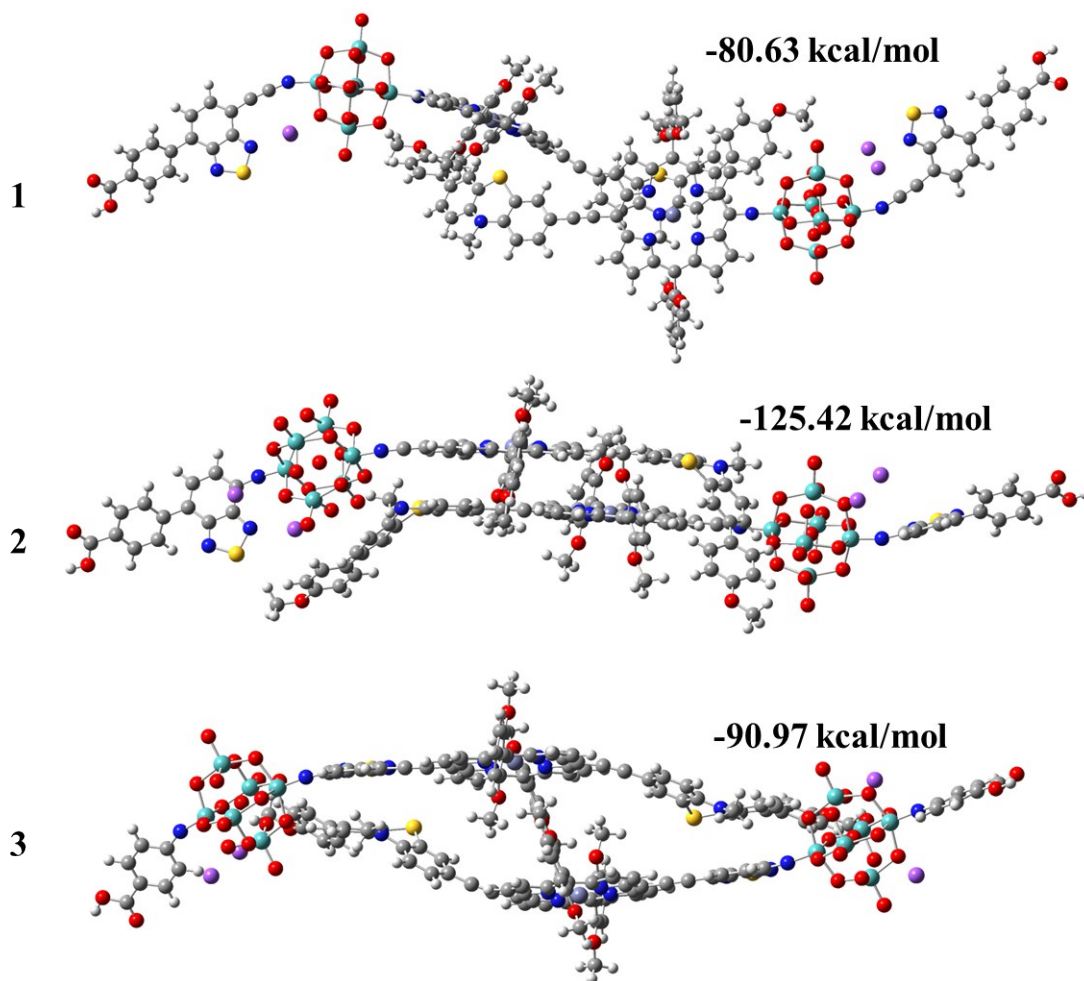
-80.63 kcal/mol

-125.42 kcal/mol

-90.97 kcal/mol

Figure S6. The optimized most stable dimer structures as well as the interaction energies ΔE_{tot} for studied dyes.
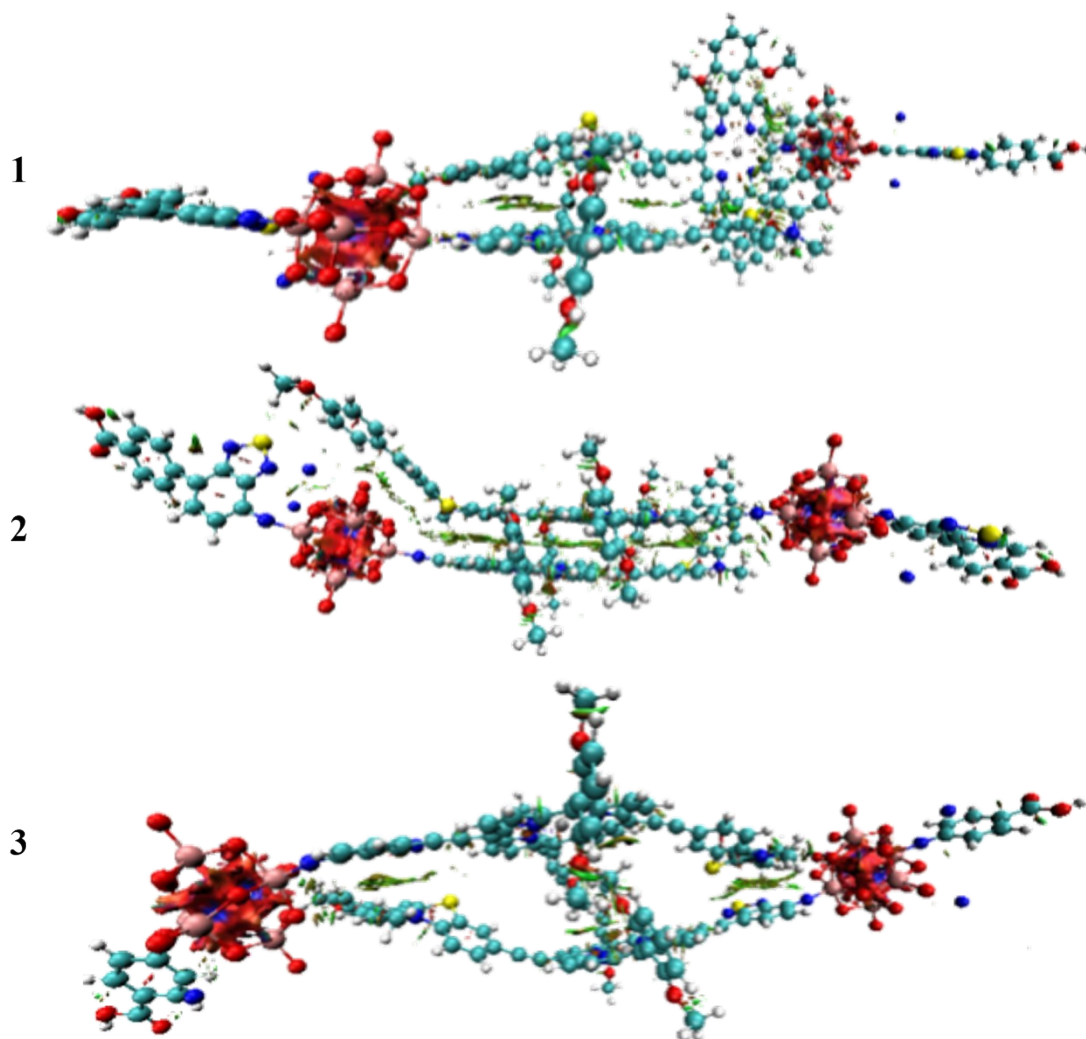
1

2

3

Figure S7. The plot of gradient isosurfaces with RDG = 0.5 a.u. for studied dyes dimers.

Table S1. The experimental and theoretical absorption spectra data of **XW11**.

XW11	λ_{max}(nm)	f
Exp.	465	—
	683	—
PBE0	455	1.00
	705	1.64

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

dye	ΔE_{CB}	n_{CT}	V_{EL}
1	−0.009	1.16	−0.28
2	−0.012	1.25	−0.30
3	−0.041	1.34	−0.34