Supporting Information for

Modeling Charge Recombination in Dye-Sensitized Solar Cells using First-Principles Electron Dynamics: Effects of Structural Modification

*Wei Ma, † Yang Jiao, † Sheng Meng†**

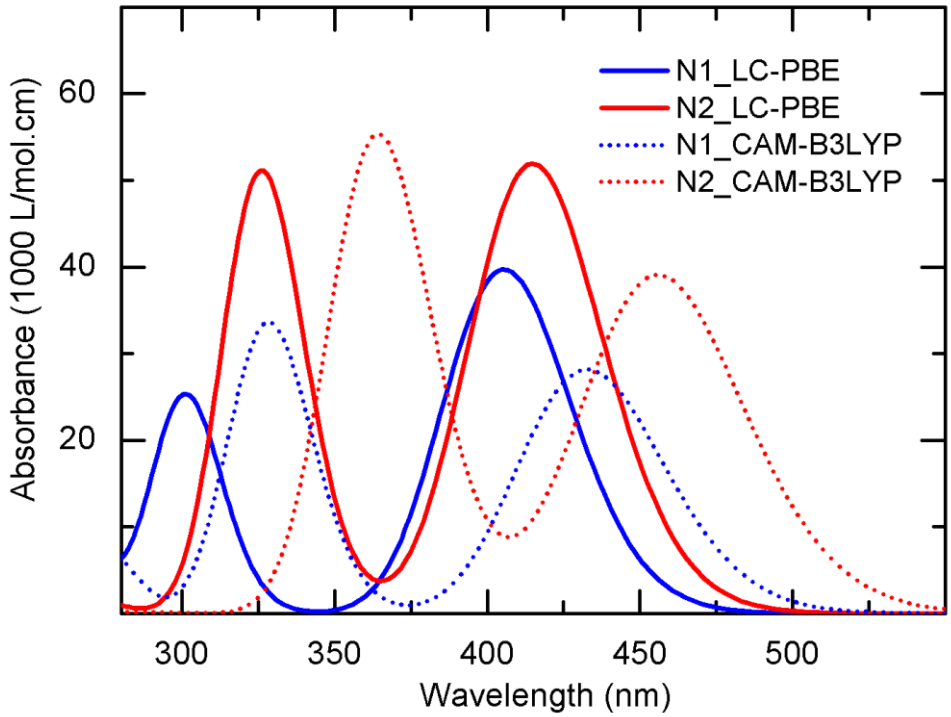

Figure S1. Calculated UV-vis absorption spectra of dyes N1 and N2 using LC-PBE/6-31G(d) and CAM-B3LYP/6-31G(d) as implemented in Gaussian.

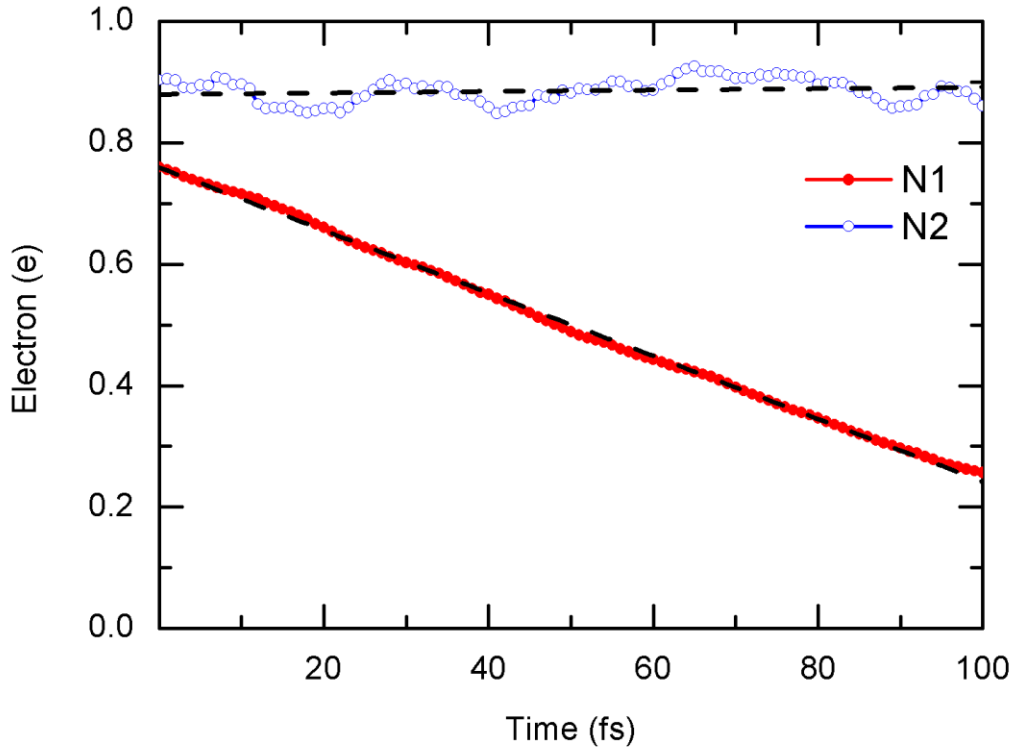

Figure S2. Fraction of electrons transferred from the TiO_2 semiconductor substrate to the organic dye during the recombination process at the organic dye-TiO_2 interface using surface hopping method implemented in VASP. The black dashed lines are results fitted by a linear decaying dynamics. Here, the ab initio molecular dynamics is performed at the ground state DFT level using plane-wave bases, ultrasoft pseudopotentials and the PW91 functional. The system is initially optimized to its energy minimum by static relaxations; then heated to 350 K with a 100 fs MD run, and stays at 350 K for 1000 fs to reach thermal equilibrium. Finally, another 1000 fs microcanonical MD production run is performed to compute the necessary electronic structure information for which the electron dynamics can be determined. In the electron dynamics simulations, 100 MD trajectories each 100 fs long are used to calculate the ensemble average. These 100 trajectories are chosen from the production MD run with 100 different starting points. For each trajectory, the TDDFT equation is integrated with a time step of 10^{-3} fs.

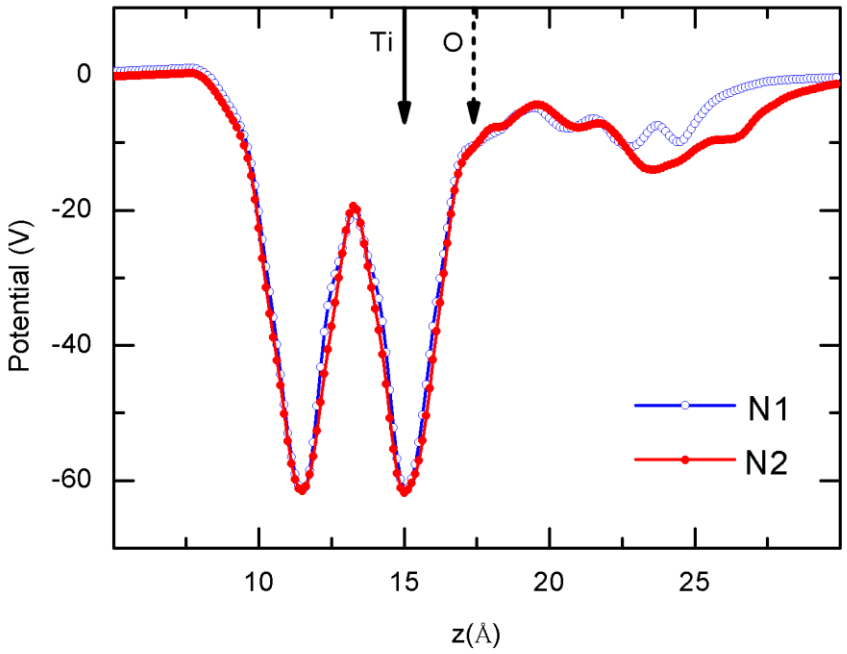

Figure S3. Calculated average values of electrostatic potentials of dyes N1 and N2 adsorbed on TiO_2 in the vertical direction. The solid and dashed arrows show the position of the interface Ti layer and the O atom of the anchoring carboxyl group.

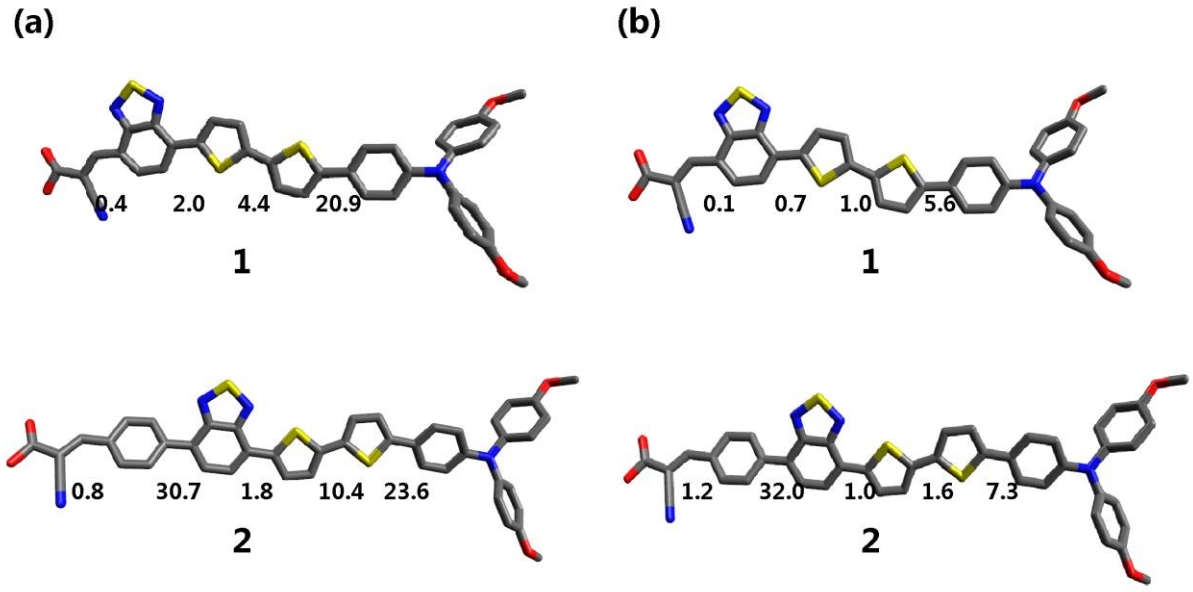

Figure S4. Geometry optimized structure of the (a) neutral and (b) cationic species of dye 1 and 2 with the dihedral angles between each plane.

Table S1. Dihedral angles, theta, between the anchoring group and the benzothiadiazole unit of relaxed structures of the neutral and cationic species of dyes 1, 2, N1 and N2 optimized using SIESTA and GAUSSIAN.

Theta/degree		Dye			
		1	2	N1	N2
SIESTA	Neutral	0.2	27.2	0.3	22.0
	Cationic	0.9	33.0	0.7	20.9
GAUSSIAN	Neutral	0.4	32.0	0.0	33.2
	Cationic	0.1	33.6	0.0	24.1