# Modeling Dye Sensitized Solar Cells: From Theory to Experiment

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# Supporting Information

**Computational Details**

Molecular calculations were carried out with the Gaussian09 code. A hybrid Hartree-Fock/ Density Functional model, referred as PBE0 was used. This functional has been chosen as it has recently been proven to yield reliable valence excitations in organic dyes and, provided that limited through space character is present, also for excitation with charge transfer character.

Structural optimizations and subsequent frequency calculations for the ground state were performed using an all electron Pople double zeta basis set with one polarization function on heavier atoms (6-31+G(d)). Vertical excitations were computed by the means of TD-DFT at the same level of theory adding diffuse and polarization functions on hydrogen atoms (6-31++G(d,p) basis). Bulk solvent effects were included using the Polarizable Continuum Model (PCM) of Tomasi and co-workers. More specifically, the Conductor-like PCM model as implemented in Gaussian (CPCM) was applied and ethanol was considered as solvent in analogy with the experimental medium. Default radii (from the UFF, scaled by 1.1) were used for structural optimizations. Two explicit ethanol molecules were placed near the $NH_2$ group of **B1** and **F1**, since this group makes hydrogen bonding to protic solvents influencing the UV-Vis spectra.

Periodic calculations were carried out with the *ab initio* CRYSTAL09 code, making use of localized (gaussian) basis sets and solving self-consistently Hartree-Fock and Kohn-Sham equations thus allowing the efficient use of hybrid functionals for band structure calculations. The crystallographic surface {101} of $TiO_2$ anatase was considered. A periodic slab model was used to study the adsorption of the dyes, characterized by two lattice parameters $a$ and $b$ along the <2-10> and <001> directions. The surface was fully passivated by co-adsorption of water molecules, as previously reported in literature for ZnO based cells[1]. 5x4 supercells were

used with a slab thickness of 12 atomic planes along the aperiodic direction <101>. Sampling

of the irreducible brillouin zone was done with 1 k-point (Γ point).

An all electron basis sets with 7-311G(d), 8-411G(d), 6-21G(d) and 511G(p) and 5-11G(d)

contractions for N, O, C and H was used to describe the dye. Durand and Barthelat large core

pseudopotential with (31/31) contractions have been used for O atoms of the $TiO_2$ substrate

and water molecules, while large core Hay and Wadt pseudopotentials with (1/1/41)

contraction have been considered for Ti atoms. The 31G(p) all electron basis set was applied

to the H atoms of water molecules.

Periodic calculations were performed at DFT level applying the hybrid exchange correlation

functional PBE0 previously used for molecular calculations.

During the dye adsorption, all the adsorbed molecules (dye and water) were allowed to fully

relax, as the six outermost atomic planes since surface relaxation of this substrate is known to

mainly involve only the outermost planes. The cell parameters $a$ and $b$ were optimized on a

hydrated surface of $TiO_2$, without dye, and were not allow to further relax.

The IPCE simulation is performed as follows.

The starting point is a computed TD-DFT absorption spectrum of a compound, consisting on

a set of transitions characterized by a position, $\lambda_i$, and an oscillator strength, $f_i$.

1- A Gaussian function is used to convolute each electronic transition. This function is

characterized by a full width at half maximum (FWHM) defined as follows :

$$g_i(\lambda) = \frac{f_i}{\sigma\sqrt{2\pi}} e^{-\frac{(\lambda-\lambda_i)^2}{2\sigma^2}} \tag{1}$$

$$FWHM = 2\sqrt{2\ln 2}\,\sigma \tag{2}$$

2- All Gaussian functions are summed to give the IPCE spectrum (eq. 3). The value of S is chosen equal to the injection efficiency computed as the fraction of spin density of the reduced dye/TiO$_2$ system computed to be localized on the TiO$_2$

$$IPCE(\lambda) = S\sum_i g_i(\lambda) \qquad (3)$$

The IPCE simulated for the dyes **B1**, **B2** and **F1** are depicted reported in Figure 5 of the manuscript. A FWHM of 0.35 eV was used.

**Experimental setup.**

The **B1**, **B2** and **F1** pyridinium based molecules were already described in the references[1].

The mesoporous TiO$_2$ substrate was obtained by a procedure detailed in ref[2–4].

Before dye adsorption, the TiO$_2$ sample was dried at 150°C for 1h. Then it was immersed over a night in a 0.5 mM solution of dye in ethanol at room temperature. Cholic acid was co-adsorbed by adding 1 mM of this molecule in the dye solution.

The cells were built by assembling the photoanode (i.e. the titanium oxide sensitized by the one of the dyes) and a counter electrode (a platinized FTO-glass substrate). The illuminated area was fixed at 0.20 cm². Three electrolytes are tested in the present publication. The electrolyte contained 0.3 M of tetrabutylamonium iodide, 0.3 M of lithium iodide and 0.05 M of iodine in acetonitrile. The photovoltaic performances of the devices were recorded under 100 mW/cm² simulated AM1.5 solar light illumination immediately after cell assembling.

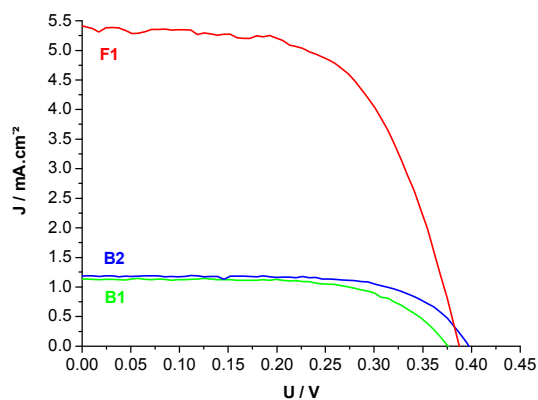The *J-V* characteristics, under AM1.5 solar light illumination, are reported in Figure SI-1

**Figure SI-1: J-V experimental characteristics of dyes B1 (green), B2 (blue) and F1 (red) adsorbed on TiO$_2$.**

## Bibliography

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