Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Electronic and Optical Properties of the Triphenylamine-Based Organic Dye Sensitized TiO_2 Semiconductor: Insight from First Principles Calculations

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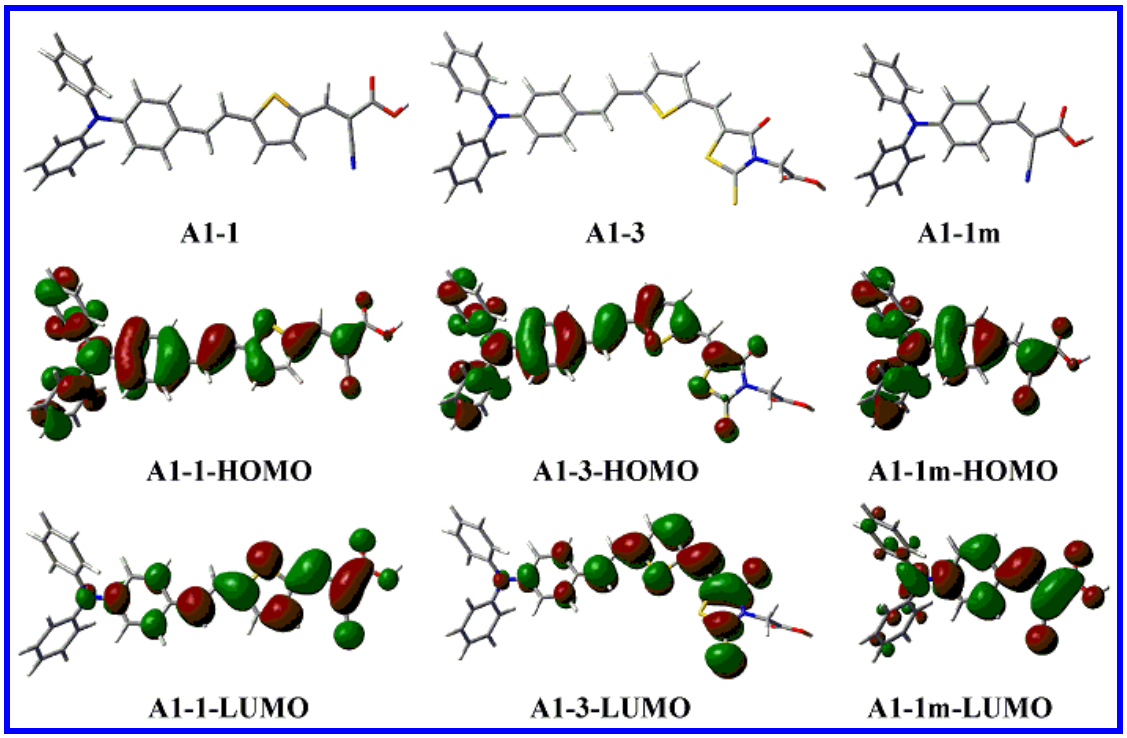


Figure S1. The selected molecular orbitals of A1-1, A1-3 and the simplified molecule A1-1m structures.

A reasonable simplified approximation in A1-3 structure has been made, as Figure

S1 shows, obviously, almost no changes in the electronic density on the triphenylamine group and the cyanoacrylic acid group of HOMO and LUMO for A1-3 and the simplified A1-1m. Following, by using this simplified dye A1-1m, we investigate the different adsorption modes on the surface of TiO_2 and the most stable adsorption configuration has been presented on the Figure S2.

The adsorption energy for these configurations can be estimated by:

$$E_{adsorption} = E_{total} - E_{A1\text{-}1} - E_{TiO_2}$$

where $E_{adsorption}$ is the adsorption energy of dye, E_{total} is total energy of the dye+TiO_2 system, $E_{A1\text{-}1}$ is the total energy of isolated dye and E_{TiO_2} is the total energy of the slab structure of TiO_2 without adsorbing dye.

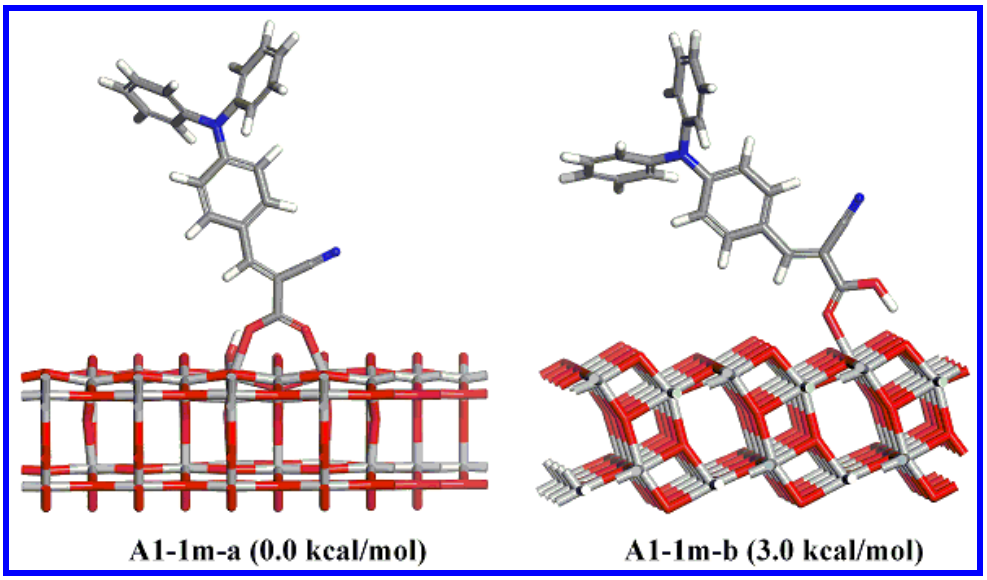
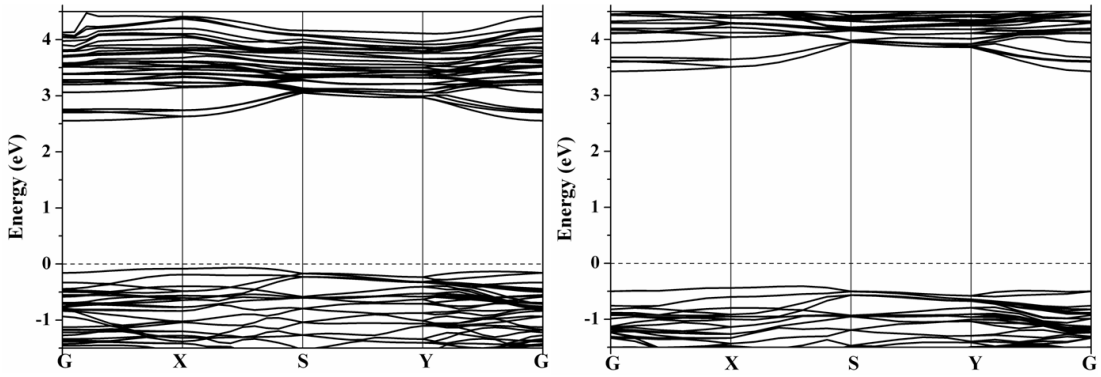


Figure S2 The different adsorption modes on the surface of TiO_2 for A1-1m-a and A1-1m-b structures.

The different band structures calculated by the pure density functional GGA-PBE and the hybrid functional HSE06 are displayed in Figure S3. As Figure S3 shows, the energy band gaps are 2.62 eV and 3.84 eV, corresponding to the results calculated by GGA-PBE and HSE06, respectively. The error caused by pure GGA-PBE is about 1.2 eV.



TiO_2 (GGA-PBE) **TiO_2 (HSE06)**

Figure S3. Comparison of the band structures calculated by GGA-PBE and HSE06 for bare TiO_2 slab structure.

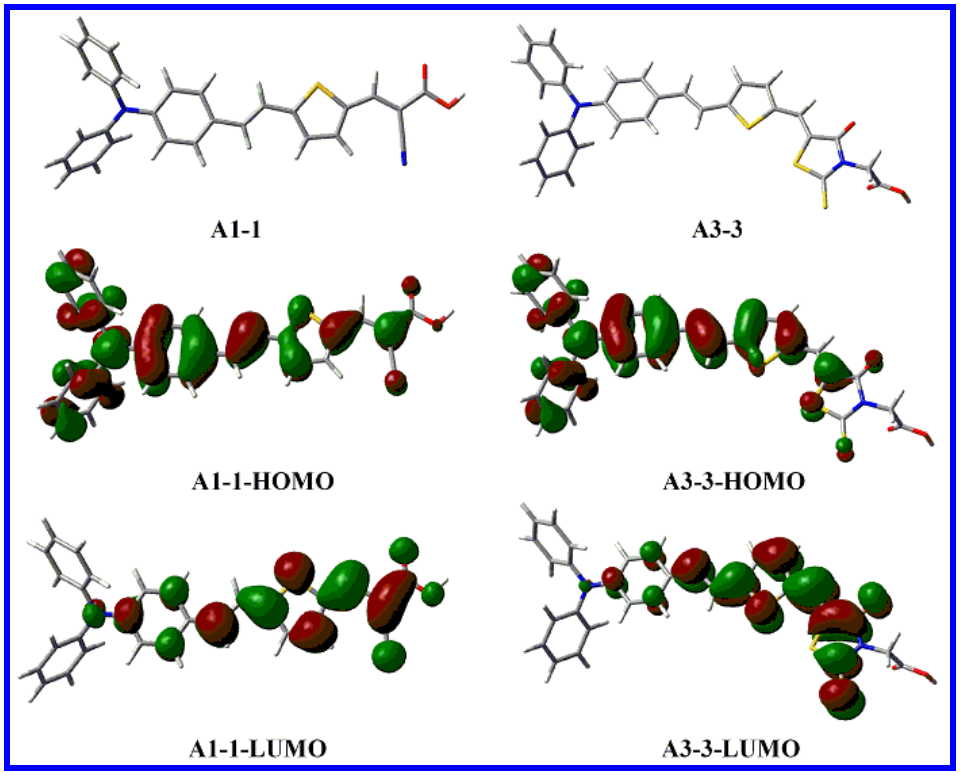


Figure S4. The selected molecular orbitals of A1-1 and A3-3 structures in MeCN.

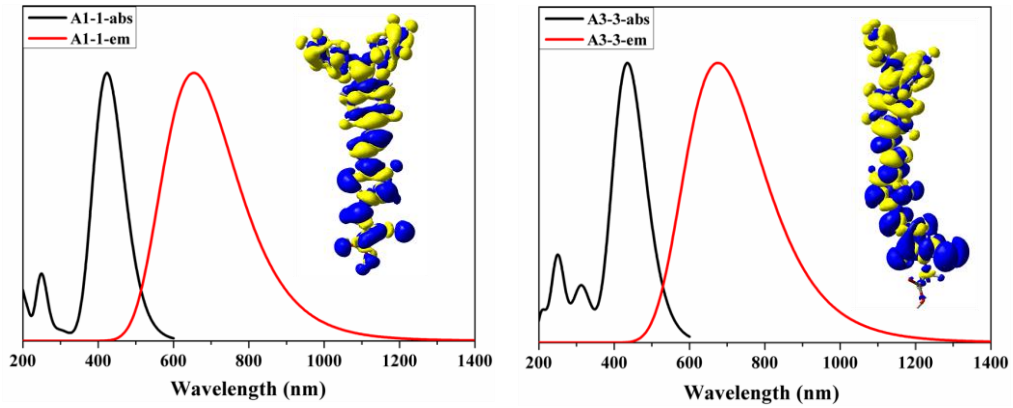


Figure S5. Normalized absorption (black) and emission spectra (TD-DFT/6-31G(d), red)for A1-1 and A3-3 (in MeCN), along with the computed difference in electronic density between the first excited state and the ground state (blue and yellow refer to an increase and a decrease of electronic density, respectively; isovalue 0.0004 au).

Table S1. The HOMO-LUMO Energy gap (E_g), transition energy (λ), excited state and a few comparative peaks, oscillator strength (f) of A1-1 and A3-1 structures and solvent.

Molecular	**$-E_{HOMO}$**	**$-E_{LUMO}$**	**E_g**	**λ/nm(ev)**	**Excited state**	***f***
A1-1	5.07	2.77	2.30	423(2.93)	117 (HOMO)→118 (LUMO)	1.9710
A3-3	5.01	2.83	2.18	435(2.85)	144 (HOMO)→145 (LUMO)	2.0121

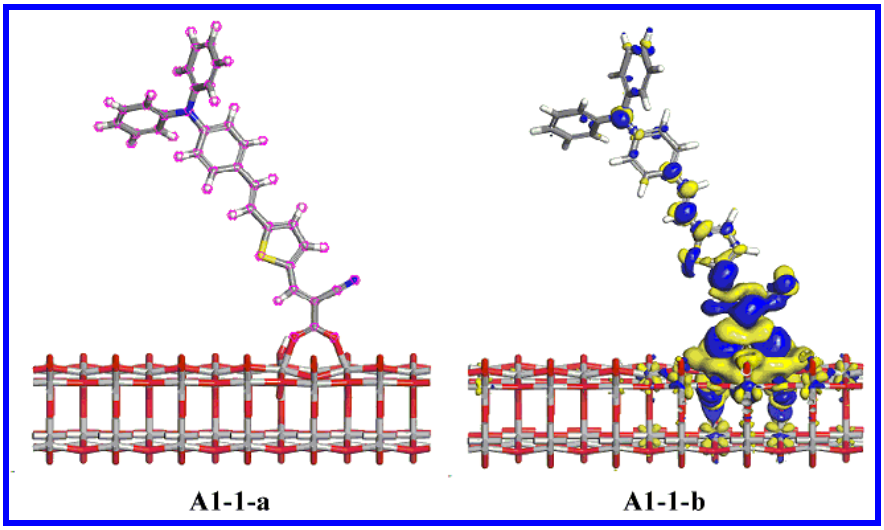


Figure S6. Optimized structure of A1-1-a (A1-1+TiO_2) and the computed difference in electronic density A1-1-b between the defferent two fragments(blue and yellow refer to an increase and a decrease of electronic density, respectively; isovalue 0.004 au), where the first fragment is the molecule adsorbed on the surface of TiO_2 (pink circle) and the second fragment is TiO_2 (101).

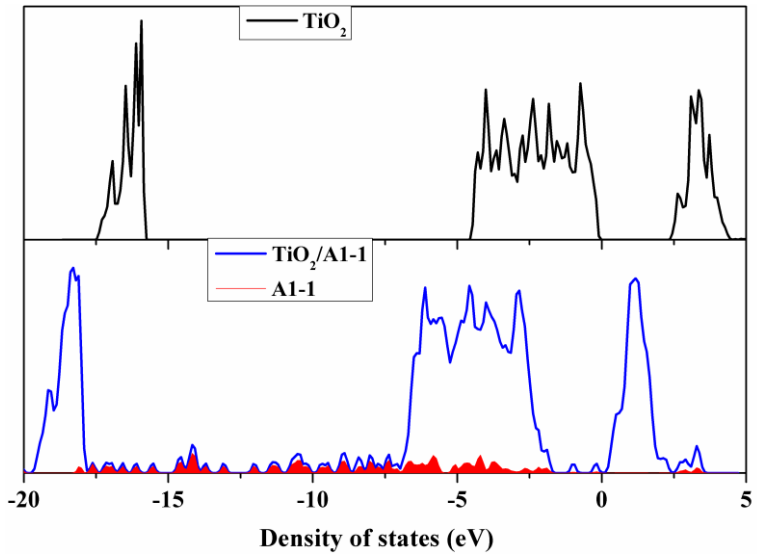


Figure S7. The calculated density of states (DOS) of isolated TiO_2 (101) (the black line), the structure A1-1+TiO_2 (the blue line) and the A1-1 dye (the red area) on the surface of the TiO_2 (101).

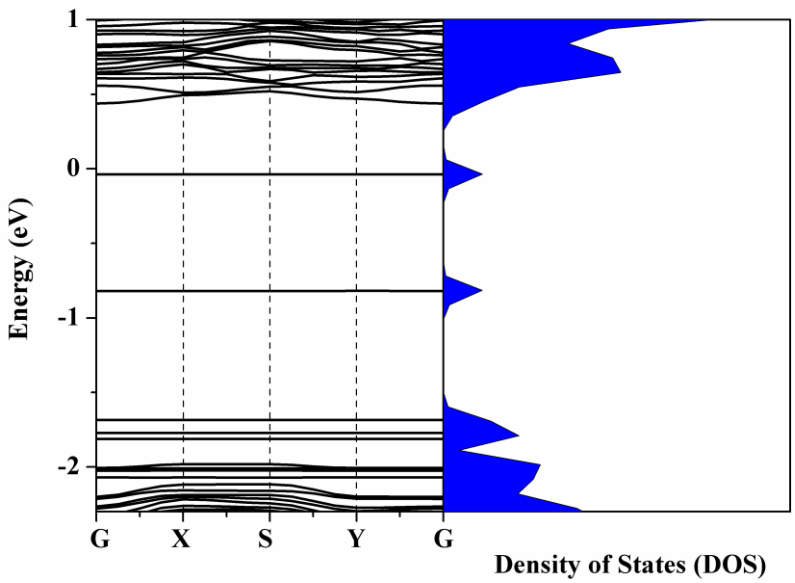


Figure S8. The band structures and the density of states (DOS) of A1-1+TiO_2 structure.

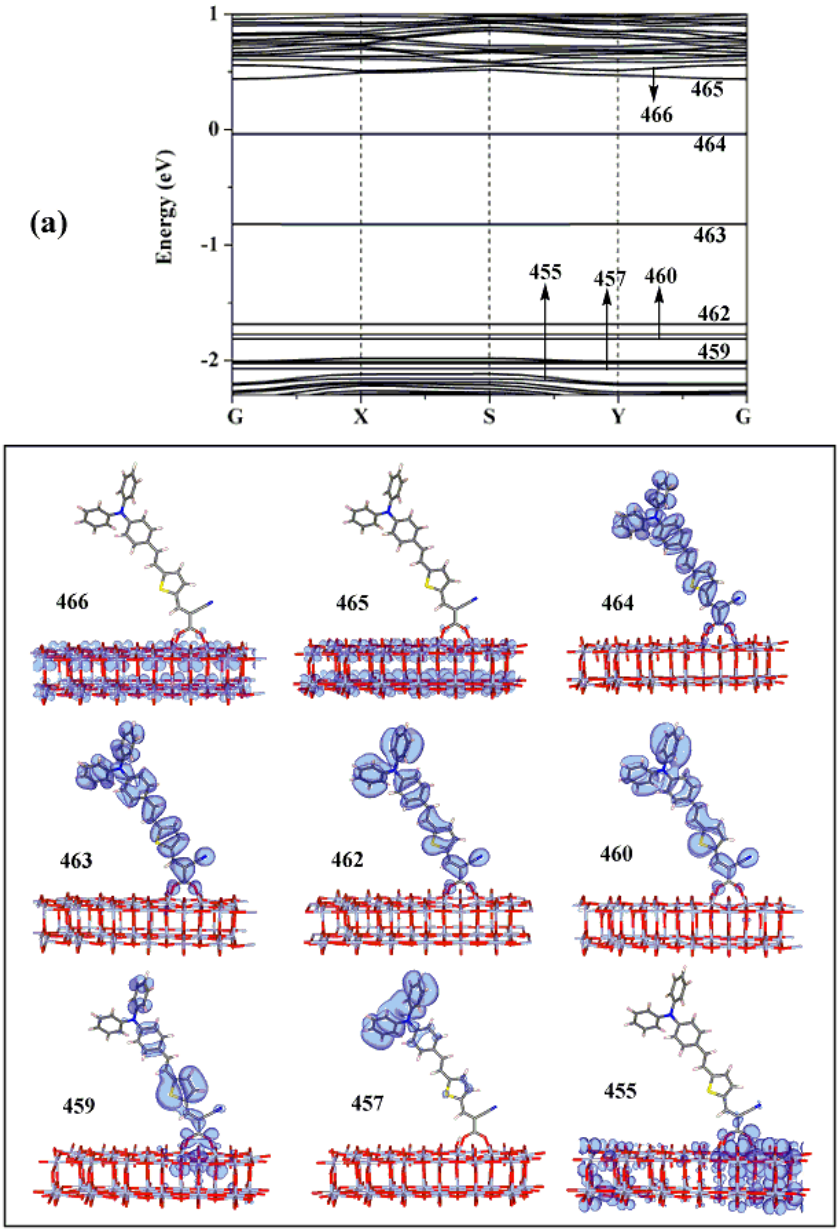


Figure S9. The band structure (**a**) of A1-1+TiO_2. The partial charge densities (isovalue 0.0004 au) for the Gamma point of the 455, 457 and 459-466 bands corresponding to the indentified band structures, respectively.

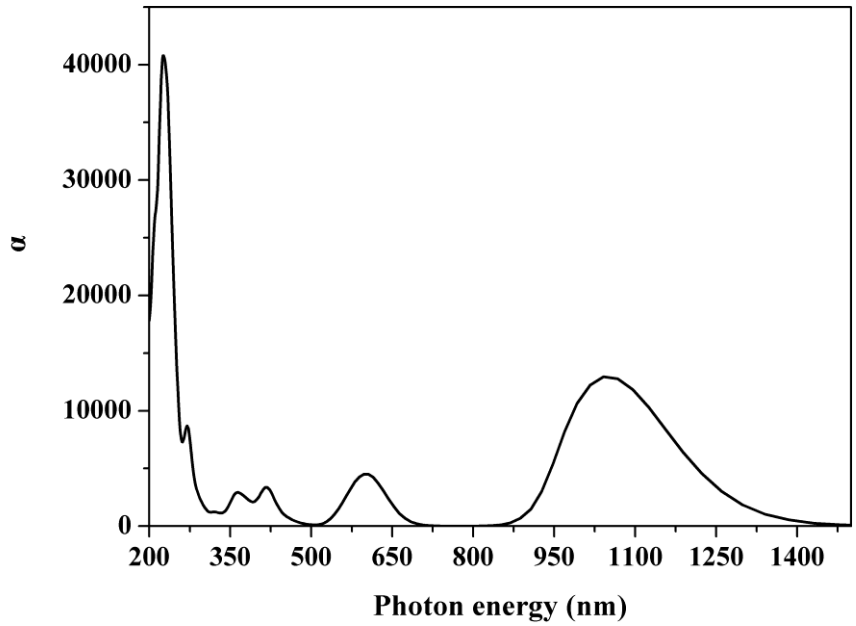


Figure S10. The predicted optical properties of the systerm (A1-1 molecule adsorped on the surface of TiO_2), the absorption coefficient $\alpha(\omega)$ as a function of the photon energy.