Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information (SI)

Theoretical Study on the Interaction of Iodide Electrolyte/Organic Dye with the TiO_2 Surface in Dye-Sensitized Solar Cells

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Computational approaches for Anatase Bulk and Surface TiO_2

The bulk anatase TiO_2 calculations have been performed with a Monkhorst-Pack k-point mesh of (10×10×4).[1, 2] The lattice parameters have been calculated by letting the ion position, cell shape, and volume to vary during minimization. For the bulk anatase TiO_2, benchmark calculations have been carried out for testing the convergence of the cutoff energy values. The lattice parameters are calculated to be a = b= 3.8005 Å, c = 9.4887 Å, which agree well with the experimental results (a = b = 3.7848 Å, c = 9.5124 Å).[3] The calculated and experimental lattice constants are given in Figure S1. Therefore, a plane-wave cutoff energy of 400 eV has been decided by comparing the total energy and lattice constants from experiments. Concerning the vacuum space of the super cell, each slab is separated from its periodic images by a vacuum gap of 40 Å, which introduced in the Z-direction to avoid the adjacent interaction. The optimized structure is given in Figure S7. Besides, a vacuum layer of ~15 Å thickness is added to avoid interactions between the top of the dye and periodic image of the slab in the vertical direction. In the present study, we have performed using the same setup, i.e., supercell, k-points, potential, and cutoff energy for entire calculations.

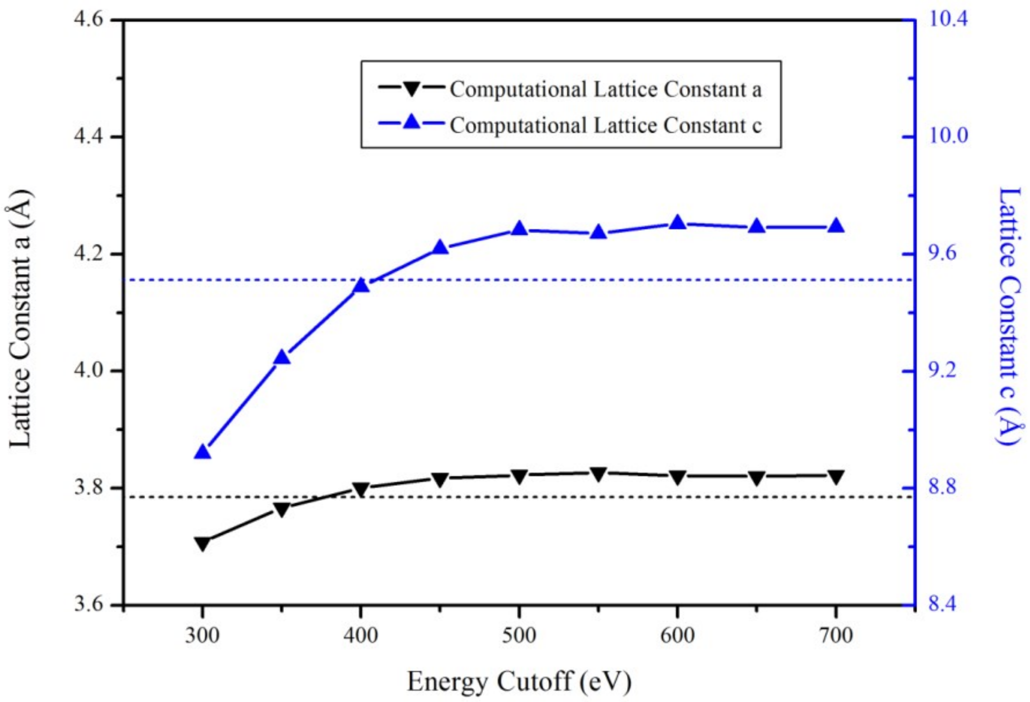


Figure S1. Calculated and experimental a) lattice constant **a**, and b) lattice constant **c** as a function of the energy cutoff (eV) for bulk TiO_2 anatase.

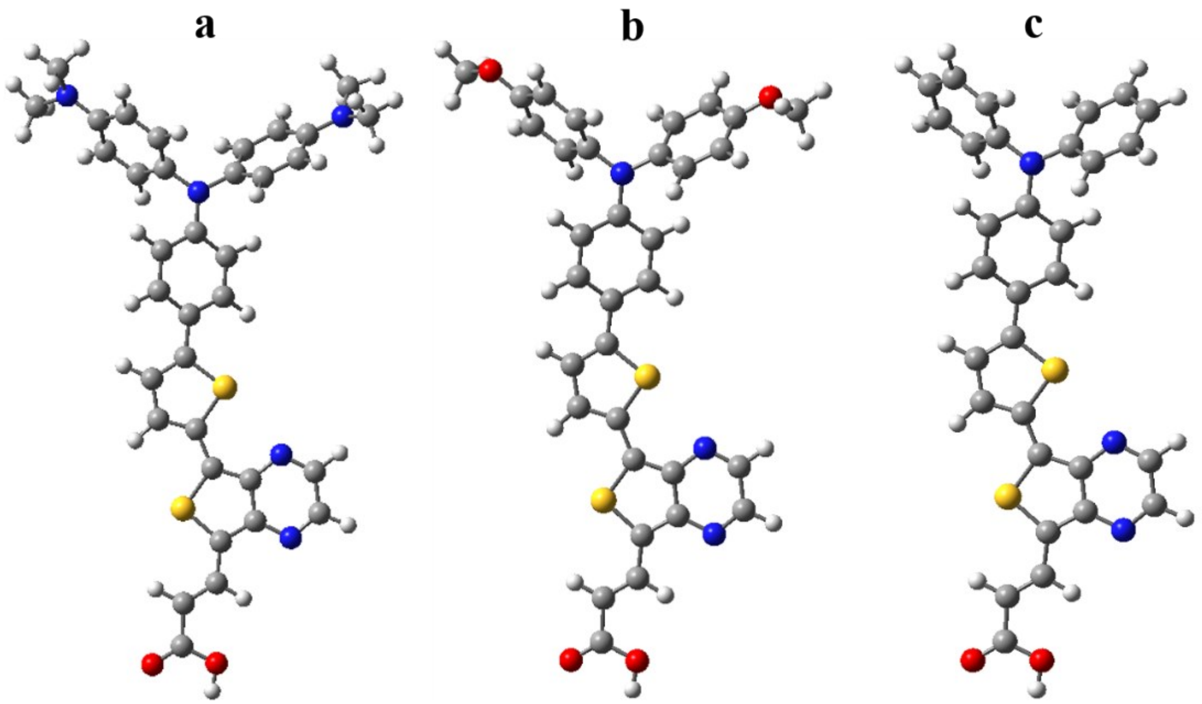


Figure S2. The optimized structure of D-π-A Organic dyes a) dimethylamino ($-N(CH_3)_2$) b) methoxy ($-OCH_3$) c) donor-free (H-) based dyes.

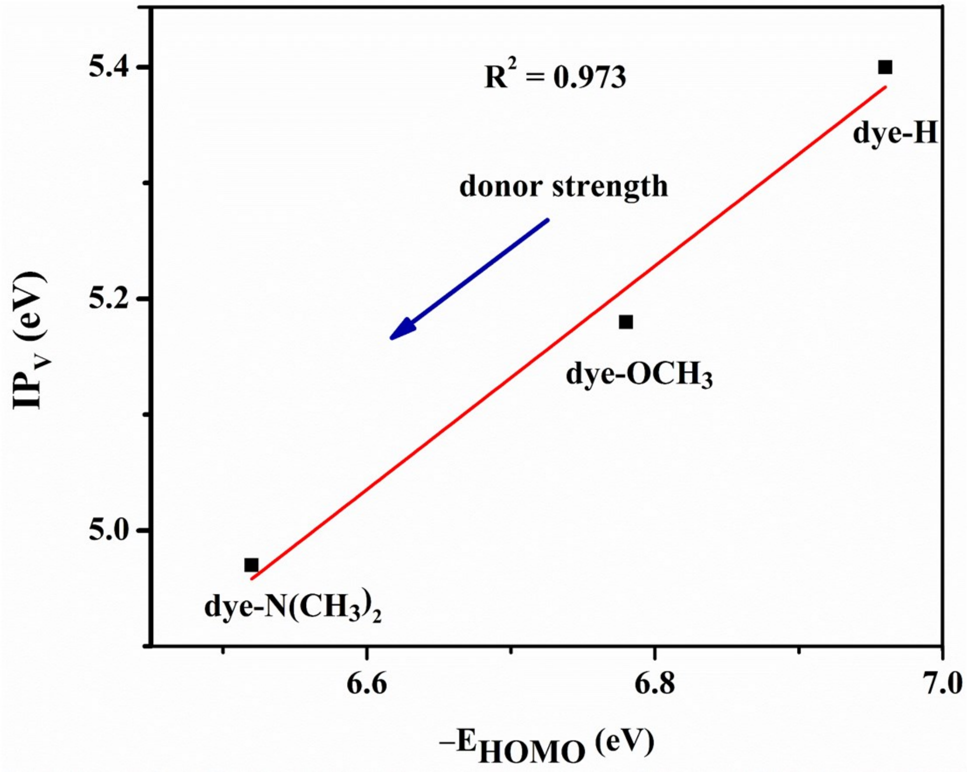


Figure S3. The Schematic illustration for the correlation between the calculated I_{PV} and E_{HOMO}. Three different donor unit are considered including dye-**N(CH$_3$)$_2$**,dye**-OCH$_3$**, dye-**H** based D−π−A dyes.

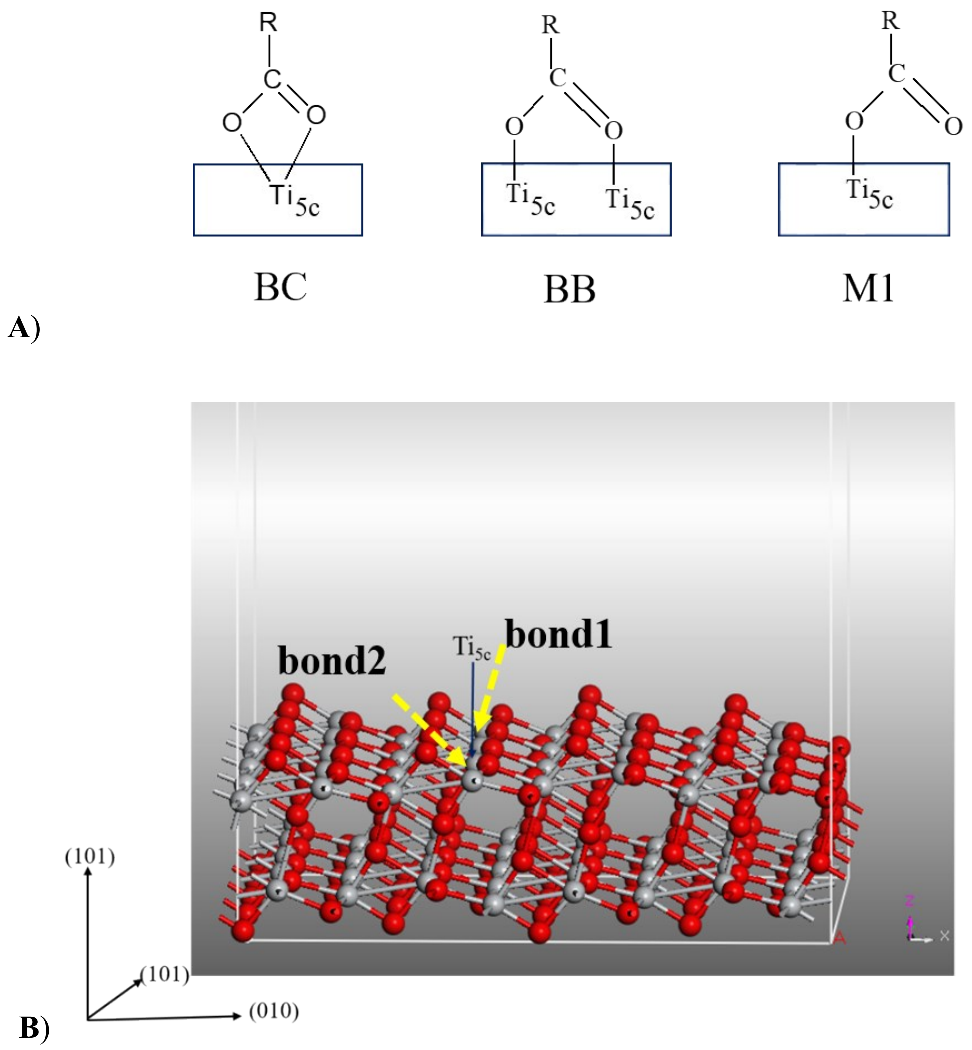


Figure S4. A) Possible adsorption configurations of the D-π-A organic dyes via carboxylate adsorption modes; bidentate chelating (BC), bidentate bridge (BB). monodentate (M1)[1] B) The side view of pristine TiO$_2$ anatase (101) surface and the corresponding to the bidentate bridge configuration, The red and grey atoms represent oxygen and titanium).[4, 5]

Table S1. Calculated Energy Levels (in eV) containing Conduction Band (CB), Fermi Level (E_F**)** and Valence Band (VB) of the studied sensitizers the [dyeI]$^-$ and [dyeI$_2$]$^{\bullet-}$ complexes on the TiO$_2$ surface.

Dyes	**H-based**			**O-based**			**N-based**		
Bands	CB	EF	VB	CB	EF	VB	CB	EF	VB
Complexes									
A1	–2.68	–3.02	–3.43	–2.58	–2.92	–3.27	–2.42	–2.75	–3.13
A1*							–2.75	–3.07	–3.42
A2	–2.68	–3.02	–3.42	–2.51	–2.85	–3.18	–2.34	–2.67	–3.09
C1	–2.48	–3.03	–3.49	–2.48	–2.81	–3.42	–2.39	–2.74	–3.09
C1*							–2.71	–3.06	–3.83
C2	–2.48	–2.93	–3.38	–2.47	–2.81	–3.13	–2.27	–2.63	–3.42
dye	–3.01	–3.35	–4.21	–2.86	–3.21	–4.01	–2.63	–2.99	–3.75
Pristine TiO$_2$	–3.83	–5.93	–6.45						

***A1 & C1**-The energy levels of **D$_1$Y** dye adsorbed onto TiO$_2$ anatase (4 × 4) slab.

Table S2. Calculated Bader charge analysis of the iodide ions with and without the [dyeI]$^-$ and [dyeI$_2$]$^{\bullet-}$ complexes on the TiO$_2$ surface.

Dyes[a]	D_1Y		D_2Y		D_3Y		D_1Y		D_2Y		D_3Y	
Sites[b]	A1	A2	A1	A2	A1	A2	C1	C2	C1	C2	C1	C2
#Atoms[c]												
$I_{(1)}$	7.38	7.39	7.18	7.37	7.15	7.23	7.02	7.01	7.05	7.01	6.98	7.15
$I_{(2)}$							6.95	7.06	6.87	6.95	6.96	6.84
$I_{(1)}$	8.00											
$I_{(1)}$-$I_{(2)}$	(7.64)-(7.36)											

[a] D_1Y, $D_2Y$and D_3Y denote the different donor unit of the dyes. [b] Sites A1, A2, C1 & C2 designate the different iodide interaction sites. [c] Atoms signify the Iodide atoms ($I_{(1)}$ for first and $I_{(2)}$ for the second iodide ion).

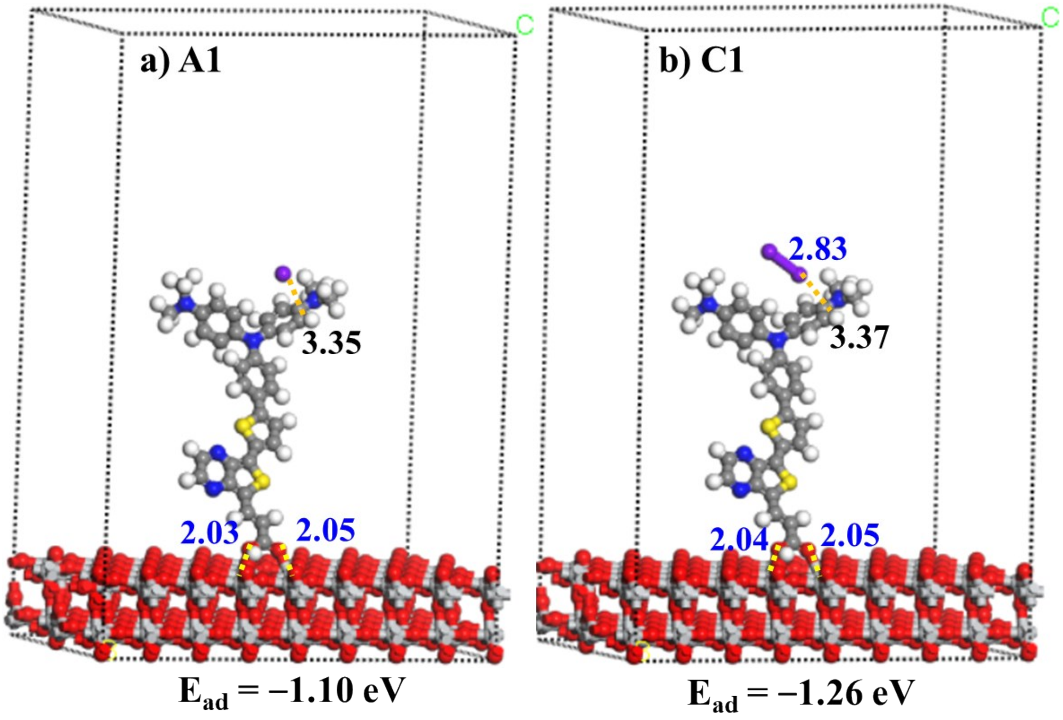


Figure S5. Optimized geometries of **(a) A1** and **(b) C1** for the dye/iodide complexes of **D_1Y** dye molecules adsorbed onto TiO_2 anatase (4 × 4) surface.

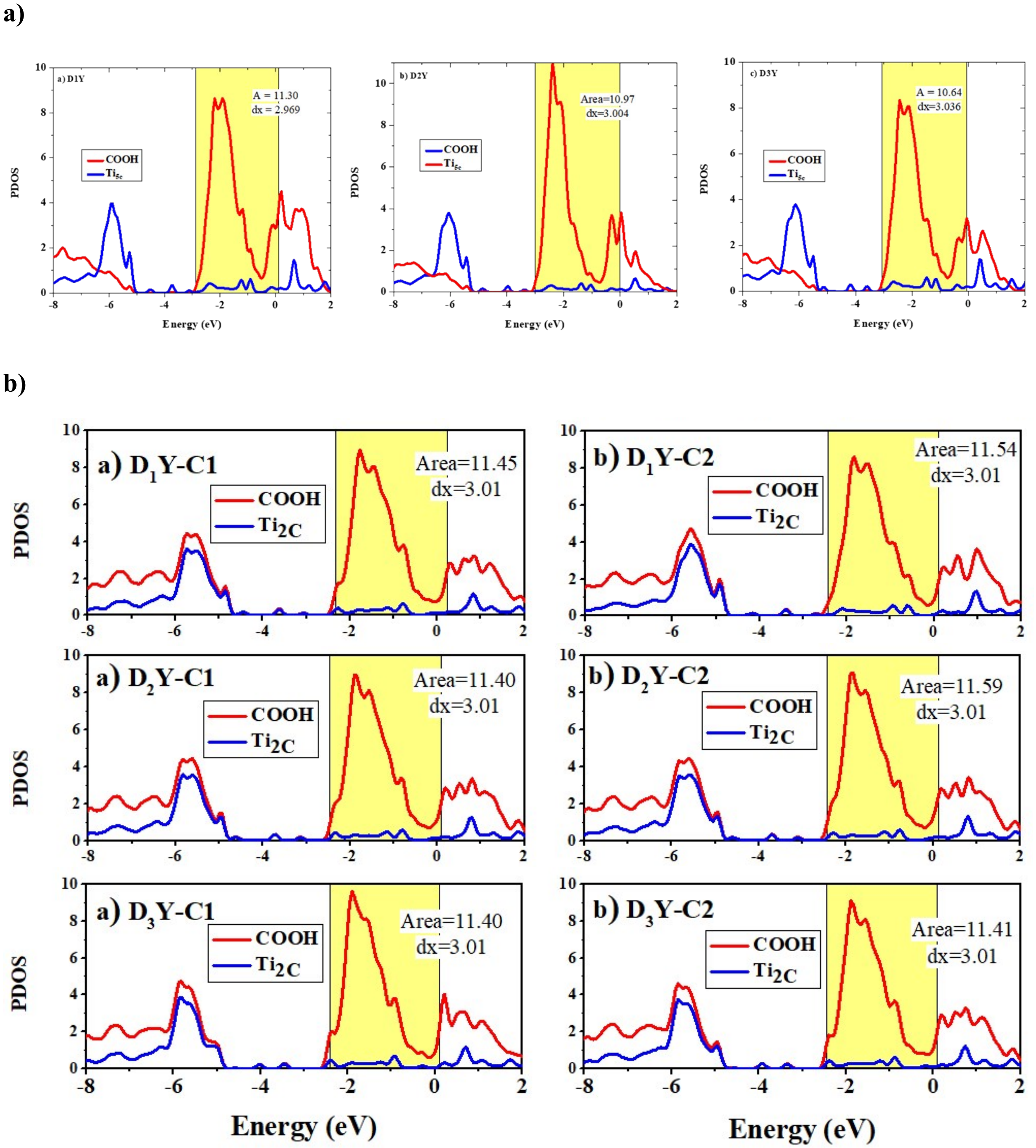
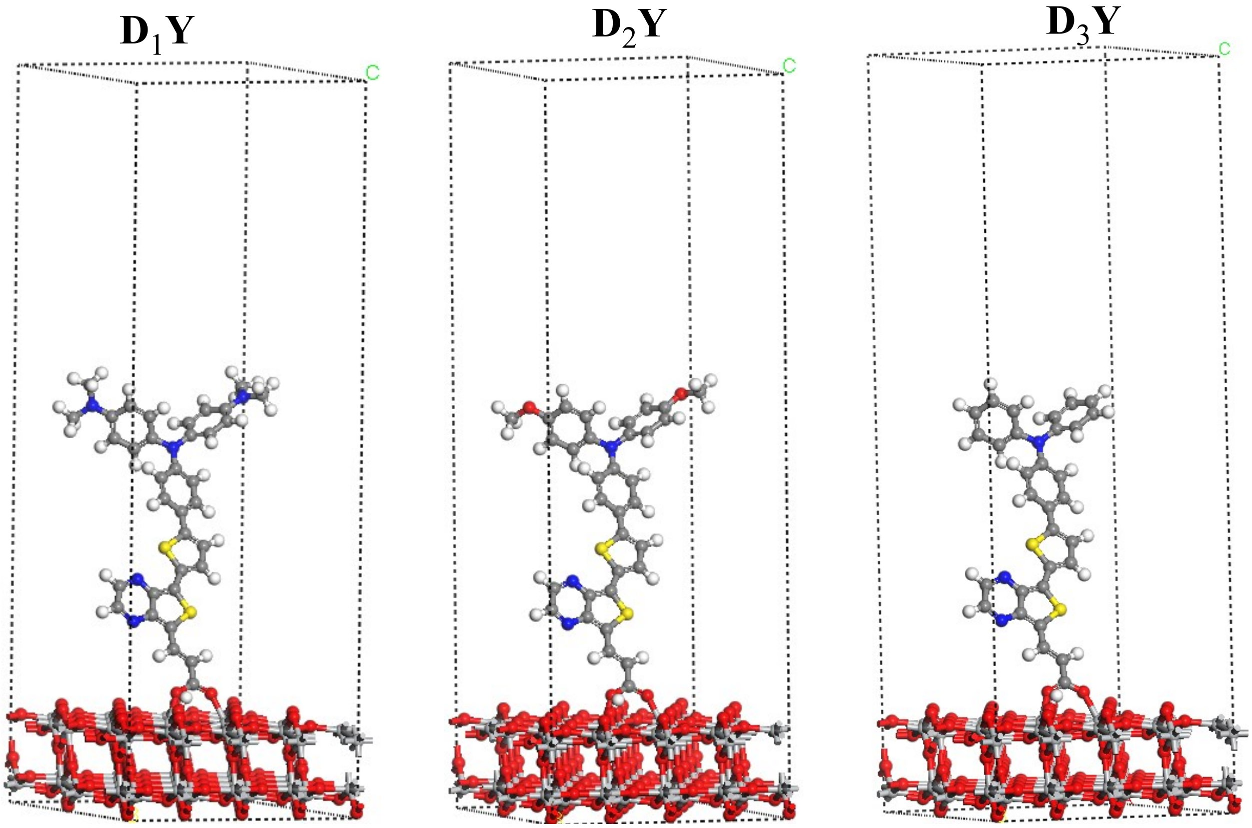


Figure S6. Calculated overlap integral between anchoring group (COOH) and two surface Ti atoms in the range of –3 to 0 eV in DOS for different donor groups (D_1Y, D_2Y & D_3Y), a) before iodide redox electrolyte interaction b) after interaction with electrolyte for $[dyeI_2]^-$configuration.



D$_1$Y **D$_2$Y** **D$_3$Y**

Figure S7. Optimized structure of D-π-A organic dye along the different donor groups a) dimethylamino- b) methoxy- c) donor-free-based onto the TiO_2 surface.

References

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