Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Molecular Engineering of Anchoring Groups for Designing Efficient Triazatruxene-Based Organic Dye-Sensitized Solar Cells

Narendra Nath Ghosh[a], Md. Habib[a], Anup Pramanik[b], Pranab Sarkar[b], Sougata Pal[a*]

[a] *Department of Chemistry, University of Gour Banga, Malda-* 732103*, India*

[b] *Department of Chemistry, Visva-Bharati University, Santiniketan-731235*

Supporting Information:

Table S1: Frontier molecular orbital energy level and the corresponding energy gaps of different studied dyes.

Dyes	$-E_{HOMO}$ (eV)	$-E_{LUMO}$ (eV)	Δ (eV)
TD1	**5.16**	**2.77**	**2.39 (2.02[a])**
TD2	**5.04**	**2.10**	**2.94**
TD3	**5.07**	**2.50**	**2.57**
TD4	**5.06**	**2.20**	**2.86**
TD5	**5.07**	**2.28**	**2.79**
TD6	**5.08**	**2.49**	**2.59**

[a] indicates the experimental value[1]

Table S2: Simulated absorption wavelengths (λ_{max} in nm), corresponding vertical excitation energies ($E_{0\text{-}0}$ in eV), oscillator strengths (***f***), light harvesting efficiency (**LHE**) and the composition of the corresponding electronic transitions (H = HOMO; L = LUMO), calculated in THF by using B3LYP/631g(d) level of theory.

Dyes	λ_{max}	$E_{0\text{-}0}$	*f*	ε (10^4)	LHE	Main compositions (contribution)
TD1	446 (476)[a]	2.80	0.81	3.69	0.84	H-2->L (99%)
	317 (318)[a]	3.90	0.48	5.20		H-6->L (48%), H-1->L+2 (16%), H->L+1 (10%), H->L+2 (10%)
TD2	469	2.64	0.90	4.67	0.875	H->L (98%)
	331	3.74	0.23	4.40		H-3->L (82%)
TD3	530	2.34	0.55	3.00	0.877	H->L (99%)
	434	2.85	0.91	4.62		H-2->L (97%)
	333	3.71	0.28	3.67		H-2->L+1 (66%), H->L+2 (18%)
TD4	483	2.56	0.78	4.12	0.911	H->L (98%)
	404	3.06	1.05	5.20		H-2->L (97%)
	317	3.91	0.20	5.10		H-1->L+1 (12%), H-1->L+2 (35%), H->L+2 (23%), H->L+3 (21%)
TD5	496	2.50	0.70	3.90	0.902	H->L (98%)
	413	3.00	1.01	4.99		H-2->L (97%)
	320	3.86	0.12	4.20		H-1->L+3 (25%), H->L+2 (16%), H->L+3 (24%), H->L+4 (14%)
TD6	530	2.34	0.56	3.00	0.90	H->L (99%)
	441	2.81	1.00	4.63		H-2->L (98%)
	363	3.42	0.32	2.66		H-3->L (37%), H->L+2 (51%)
	321	3.86	0.26	2.67		H-1->L+3 (46%), H->L+3 (14%), H->L+4 (22%)

*a indicates the experimental value[1]

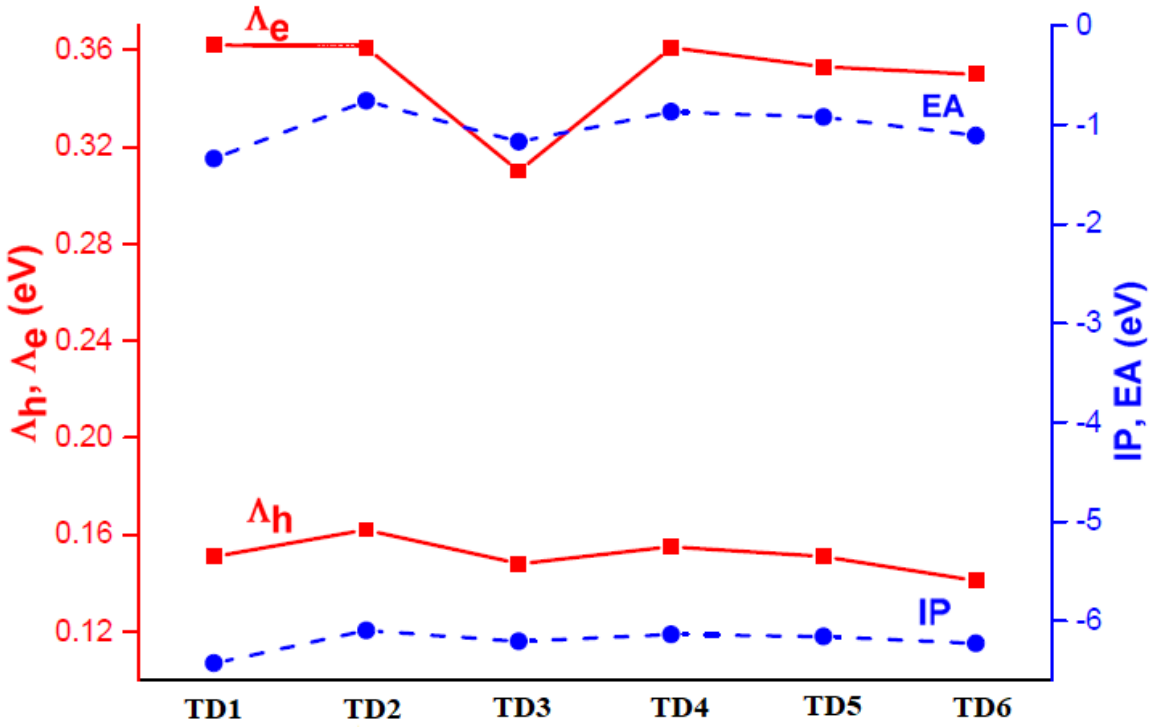

Figure S1. Computed reorganization energy (Λ_h and Λ_e), ionization energy (IP), and electron affinity (EA) of the studied dyes.

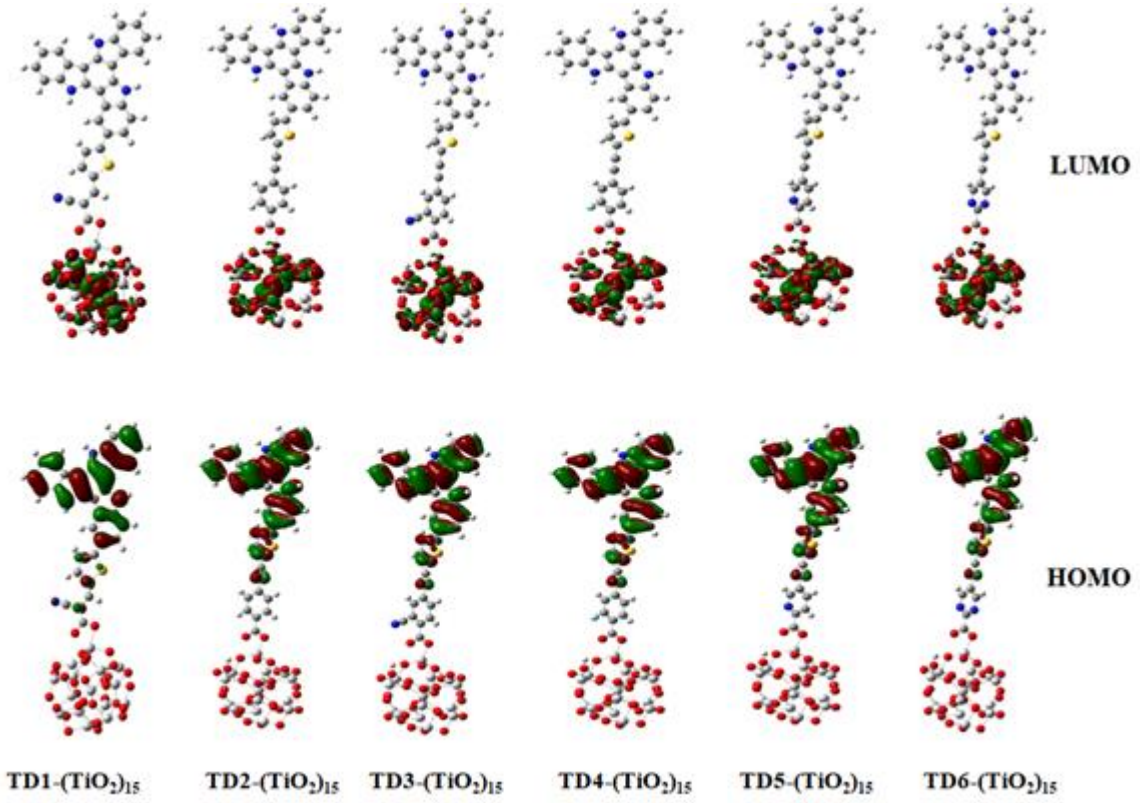

Figure S2. HOMO, LUMO isosurfaces plots of the dye-**$(TiO_2)_{15}$** nanocomposites.

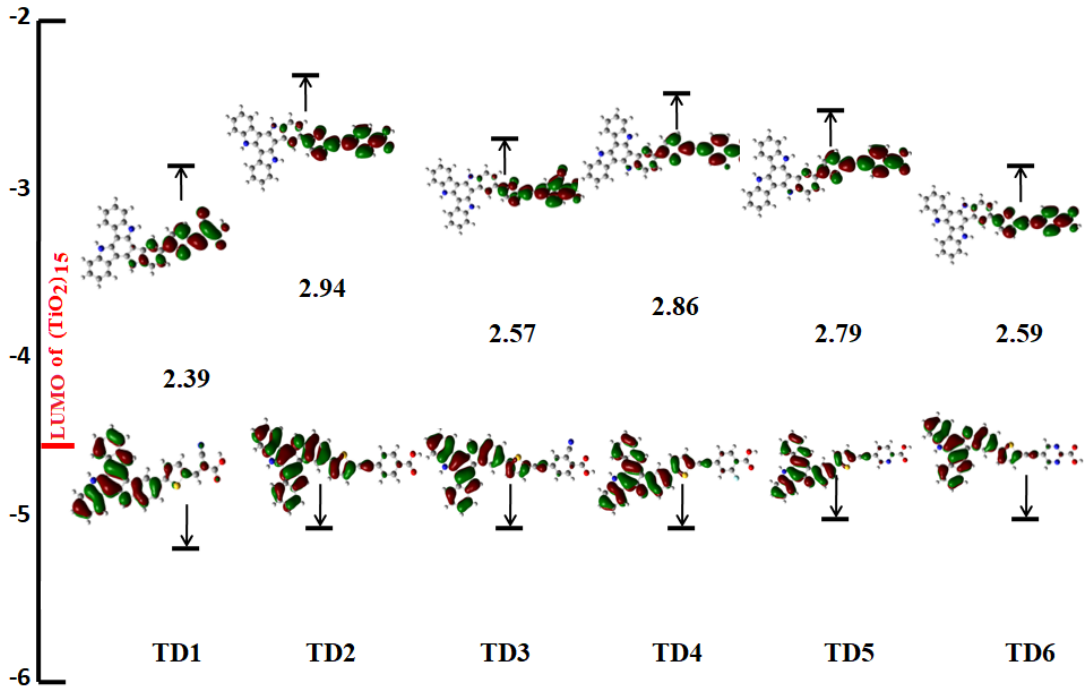

Figure S3. Isosurface plots for the HOMO and LUMO levels and calculated energy levels of **TD1-TD6**. The red horizontal solid line indicates LUMO level of $(TiO_2)_{15}$ nanocluster (-4.60 eV).

Calculation of IP, EA and reorganization energy:

The Λ for hole Λ_h and electron Λ_e transfer can be estimated[2, 3] respectively by Eq. 11 and Eq. 10:

$$\Lambda_e = [E_0^- - E_-] + [E_-^0 - E_0] \quad (10)$$

$$\Lambda_h = [E_0^+ - E_+] + [E_+^0 - E_0] \quad (11)$$

- E_0^+ and E_0^- are the energy of the cation (anion) calculated based on the optimized structure of the neutral molecule;
- E_+ and E_- represents the energy of the cation (anion) calculated based on the optimized cation (anion) structure;
- E_+^0 and E_-^0 corresponds to the energy of the neutral molecule calculated at the cationic (anionic) state;
- E_0 is the energy of the neutral molecule at the ground state.

Furthermore, the ionization potential (*IP*) and electron affinity (*EA*) corresponding to all isolated dyes are calculated by following:

$$IP = E_0 - E_0^+ \quad (11)$$

$$EA = E_0^- - E_0 \quad (12)$$

References

1. X. Qian, Y.-Z. Zhu, J. Song, X.-P. Gao and J.-Y. Zheng, New donor-π-acceptor type triazatruxene derivatives for highly efficient dye-sensitized solar cells, *Org. Lett.*, 2013, 15, 6034-6037.
2. L.-J. He, W. Wei, J. Chen, R. Jia, J. Wang and H.-X. Zhang, The effect of D–[D e–π–A] n (n= 1, 2, 3) type dyes on the overall performance of DSSCs: a theoretical investigation, *J. Mater. Chem. C*, 2017, 5, 7510-7520.
3. L.-J. He, J. Wang, J. Chen, R. Jia and H.-X. Zhang, The effect of relative position of the π-spacer center between donor and acceptor on the overall performance of D-π-A dye: a theoretical study with organic dye, *Electrochim. Acta*, 2017, 241, 440-448.