Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Can elongation of the π-system in triarylamine derived sensitizers with either benzothiadiazole and / or *ortho*-fluorophenyl moieties enrich their light harvesting efficiency? – A Theoretical Study

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Table S1 Calculated singlet excitation energies and oscillator strengths of ten dyes

Dyes	No.	Energy (cm-1)	Wavelength (nm)	Symmetry	Osc. Strength	Major contributions
A1	1	20874.579	479.05157	Singlet-A	1.7342	H-1->LUMO (18%), HOMO->LUMO (76%)
	2	29292.646	341.38261	Singlet-A	0.1577	H-1->LUMO (55%), HOMO->L+1 (23%)
	3	33239.951	300.8428	Singlet-A	0.1211	H-1->LUMO (15%), HOMO->LUMO (11%), HOMO->L+1 (59%)
	4	34177.98	292.58605	Singlet-A	0.0253	H-1->L+2 (14%), HOMO->L+2 (71%)
	5	35745.126	279.75842	Singlet-A	0.0607	H-8->LUMO (15%), H-7->LUMO (22%), H-5->LUMO (11%), H-2->LUMO (12%), H-1->L+1 (12%), HOMO->L+4 (10%)
A1-F	**No.**	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
	1	20667.293	483.85629	Singlet-A	2.2158	H-1->LUMO (17%), HOMO->LUMO (67%), HOMO->L+1 (10%)
	2	28389.299	352.2454	Singlet-A	0.0633	H-2->LUMO (10%), H-1->LUMO (23%), HOMO->L+1 (53%)

	3	31086.436	321.68371	Singlet-A	0.0595	H-1->LUMO (32%), H-1->L+1 (15%), HOMO->LUMO (27%), HOMO->L+1 (19%)
	4	33485.145	298.63989	Singlet-A	0.4634	H-2->LUMO (27%), H-1->L+1 (19%), HOMO->L+2 (21%)
	5	34030.38	293.85508	Singlet-A	0.0264	H-1->L+3 (20%), HOMO->L+3 (63%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
C218	1	20307.568	492.42726	Singlet-A	1.7771	H-1->LUMO (24%), HOMO->LUMO (70%)
	2	28289.285	353.49072	Singlet-A	0.1125	H-1->LUMO (57%), HOMO->LUMO (14%), HOMO->L+1 (15%)
	3	32338.217	309.23165	Singlet-A	0.1808	HOMO->LUMO (12%), HOMO->L+1 (60%)
	4	32743.916	305.40024	Singlet-A	0.047	HOMO->L+2 (78%)
	5	35532.194	281.43491	Singlet-A	0.0607	H-9->LUMO (10%), H-8->LUMO (13%), H-7->LUMO (13%), H-3->LUMO (17%), H-1->L+1 (13%), HOMO->L+3 (11%)
C218-F	**No.**	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
	1	20251.915	493.78046	Singlet-A	2.181	H-1->LUMO (23%), HOMO->LUMO (61%), HOMO->L+1 (10%)
	2	27857.776	358.9662	Singlet-A	0.1878	H-3->LUMO (10%), H-1->LUMO (30%), HOMO->L+1 (44%)
	3	29865.304	334.83671	Singlet-A	0.1135	H-1->LUMO (23%), H-1->L+1 (15%), HOMO->LUMO (33%), HOMO->L+1 (23%)
	4	32818.12	304.70972	Singlet-A	0.0507	H-1->L+3 (12%), HOMO->L+3 (65%)
	5	33282.698	300.45641	Singlet-A	0.3915	H-4->LUMO (14%), H-3->LUMO (16%), H-1->L+1 (21%), HOMO->L+2 (16%)
D2	**No.**	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
	1	16898.239	591.77766	Singlet-A	2.2172	H-1->LUMO (13%), HOMO->LUMO (79%)
	2	18798.494	531.95751	Singlet-A	0.0009	H-4->L+2 (10%), H-1->L+2 (12%), HOMO->L+2 (69%)
	3	23209.571	430.85674	Singlet-A	0.3094	H-3->LUMO (11%), H-1->LUMO (35%), HOMO->L+1 (37%)
	4	25691.356	389.23598	Singlet-A	0.0776	H-1->LUMO (37%), H-1->L+1 (22%), HOMO->L+1 (23%)
	5	29672.536	337.01198	Singlet-A	0.0014	H-14->L+2 (16%), H-3->L+2 (10%), H-1->L+2 (56%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
D2-F	1	16772.415	596.21706	Singlet-A	2.3914	HOMO->LUMO (76%)

	2	18218.577	548.89028	Singlet-A	0.0017	H-2->L+2 (15%), HOMO->L+2 (75%)
	3	22403.011	446.36858	Singlet-A	0.5195	H-1->LUMO (28%), HOMO->L+1 (48%)
	4	25321.951	394.91428	Singlet-A	0.0585	H-1->LUMO (46%), H-1->L+1 (27%), HOMO->L+1 (10%)
	5	29091.813	343.73932	Singlet-A	0.0006	H-1->L+2 (68%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
Y123	1	20486.624	488.12337	Singlet-A	1.8624	H-1->LUMO (27%), HOMO->LUMO (64%)
	2	28223.954	354.30897	Singlet-A	0.143	H-3->LUMO (12%), H-1->LUMO (45%), HOMO->LUMO (15%), HOMO->L+1 (18%)
	3	32216.426	310.40066	Singlet-A	0.2414	HOMO->LUMO (16%), HOMO->L+1 (56%)
	4	32599.542	306.75278	Singlet-A	0.9558	H-1->L+2 (13%), HOMO->L+2 (71%)
	5	33869.874	295.24763	Singlet-A	0.147	HOMO->L+3 (68%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
Y123-F	1	20326.119	491.97784	Singlet-A	2.2622	H-1->LUMO (25%), HOMO->LUMO (57%), HOMO->L+1 (10%)
	2	27649.683	361.66779	Singlet-A	0.2204	H-1->LUMO (26%), HOMO->L+1 (44%)
	3	29872.563	334.75534	Singlet-A	0.0949	H-1->LUMO (21%), H-1->L+1 (16%), HOMO->LUMO (36%), HOMO->L+1 (20%)
	4	32450.328	308.16329	Singlet-A	0.9342	H-1->L+2 (20%), HOMO->L+2 (64%)
	5	32797.149	304.90455	Singlet-A	0.5181	H-6->LUMO (17%), H-1->L+1 (22%), HOMO->L+3 (25%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
Y1234	1	16780.481	595.93048	Singlet-A	2.2196	H-1->LUMO (14%), HOMO->LUMO (78%)
	2	18714.612	534.34184	Singlet-A	0.0009	H-1->L+2 (13%), HOMO->L+2 (69%)
	3	23091.813	433.05392	Singlet-A	0.3199	H-3->LUMO (11%), H-1->LUMO (34%), HOMO->L+1 (37%)
	4	25575.211	391.00362	Singlet-A	0.0695	H-1->LUMO (36%), H-1->L+1 (22%), HOMO->L+1 (23%)
	5	29551.552	338.3917	Singlet-A	0.0011	H-14->L+2 (15%), H-3->L+2 (13%), H-1->L+2 (54%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Symmetry**	**Osc. Strength**	**Major contributions**
Y1234-F	1	16829.681	594.18833	Singlet-A	2.4786	H-1->LUMO (10%), HOMO->LUMO (75%)

	2	18353.273	544.86195	Singlet-A	0.0008	HOMO->L+2 (73%)
	3	22482.053	444.79923	Singlet-A	0.4914	H-1->LUMO (24%), HOMO->L+1 (47%)
	4	25327.597	394.82624	Singlet-A	0.0804	H-1->LUMO (43%), H-1->L+1 (26%)
	5	29286.194	341.45783	Singlet-A	0.0007	H-3->L+2 (10%), H-1->L+2 (60%)

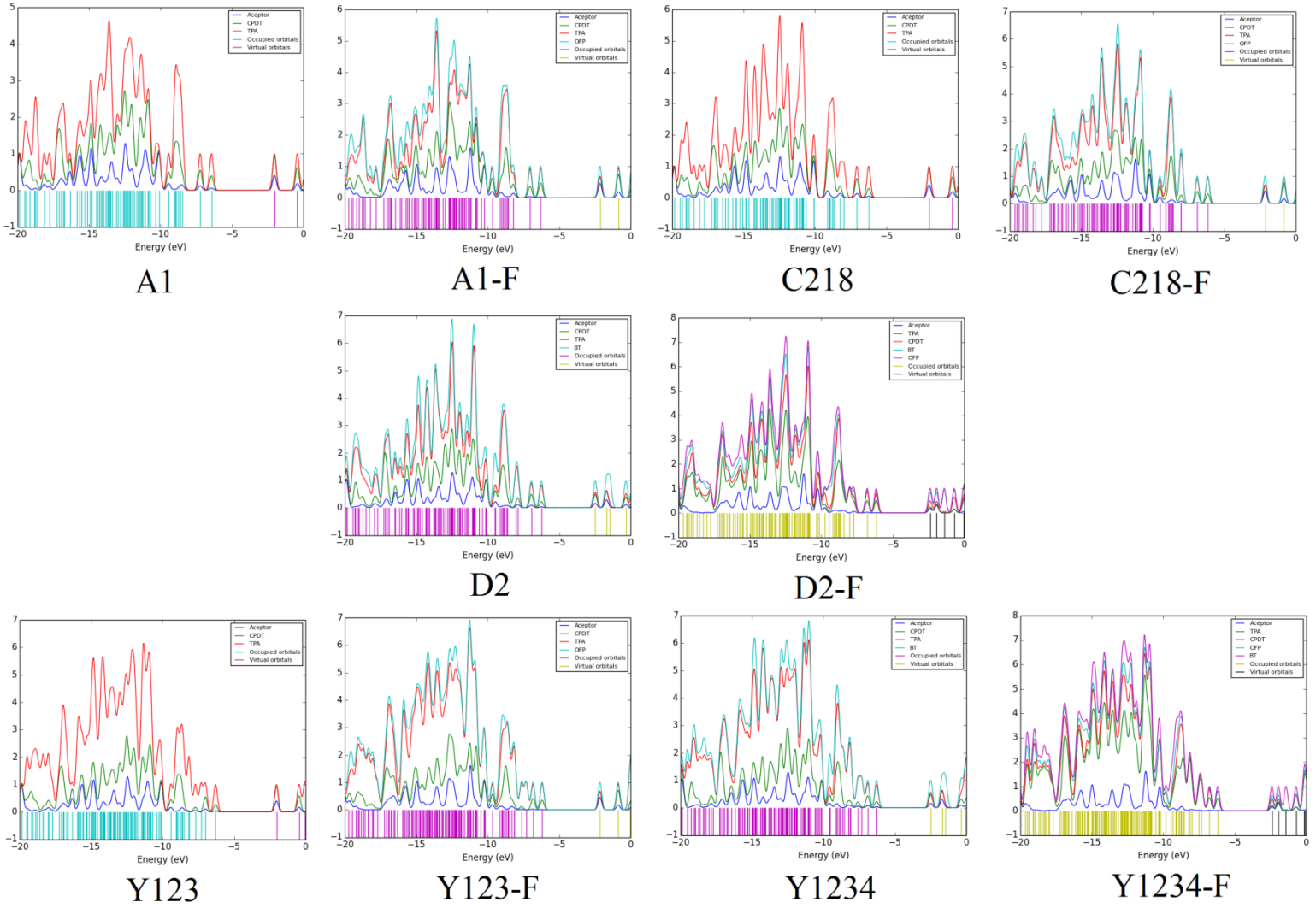

Figure S1 Calculated partial density of states (PDOS) of ten dyes

Table S2 Bond Lengths, Angles, and Dihedrals of Triphenylamine Derivatives Before (B) and After (A) Adsorption on TiO_2 slab Calculated by GGA at PBE/DNP Level[a]

Compound	State*	Bond length (Å)	Bond Angle (°)	Torsion Angle (°)		
		N – C1	Φ (C1-N-C1′)	θ1 (C1-N-C1′-C2′)	θ2 (C-C-C-S) / (C-C-C-C)	θ3 (C-C-C-S)
A1	B	1.410	120.51	34.41	14.70	--
	A	1.417	120.81	40.22	19.83	--
A1-F	B	1.413	120.40	36.12	24.35	--
	A	1.417	120.03	34.85	18.40	--
C218	B	1.404	121.09	28.67	22.37	--
	A	1.415	120.84	32.78	21.30	--
C218-F	B	1.405	120.69	27.30	25.31	--
	A	1.407	120.39	29.42	21.63	--
D2	B	1.401	120.92	27.69	0.430	0.257
	A	1.416	120.08	33.38	1.504	1.780
D2-F	B	1.403	120.84	27.80	0.276	0.681
	A	1.410	120.73	30.31	0.648	0.281
Y123	B	1.415	120.43	32.02	11.52	--
	A	1.411	120.55	33.45	11.93	--
Y123-F	B	1.416	120.70	37.06	14.84	--
	A	1.414	120.70	34.70	13.06	--
Y1234	B	1.401	120.84	29.02	1.358	0.425
	C	1.411	121.38	34.40	5.186	3.595
Y1234-F	B	1.402	120.77	29.66	1.361	0.470
	C	1.414	120.65	36.20	7.608	0.343

[a] For reference see the bond lengths, bond angle and torsion angles in figure 2.

Additional Supporting Information

Table AS1 Calculated adsorption energies using Dmol^3 at the GGA/PBE/DNP level of theory

E_{TiO2} (a.u)	E_{dye} (a.u)	$E_{dye+TiO2}$ (a.u)	E_{ads} (a.u)	E_{ads} (kcal/mol)
-27975.1	-2702.06	-30677.2	-0.03034	-19.1114
-27975.1	-3029.99	-31005.1	-0.03384	-21.3198
-27975.1	-3317.58	-31292.7	-0.03978	-25.0628
-27975.1	-3645.5	-31620.6	-0.04329	-27.2713
-27975.1	-3275.5	-31250.6	-0.02881	-18.1483
-27975.1	-3603.42	-31578.5	-0.03231	-20.3568
-27975.1	-4429.4	-32404.5	-0.0572	-36.0349
-27975.1	-4757.33	-32732.5	-0.0607	-38.2433
-27975.1	-3960.6	-31935.7	-0.03775	-23.7804
-27975.1	-4288.52	-32263.6	-0.04125	-25.9889

Table AS2 Ionization potentials, electron affinities and reorganization energies of ten dyes calculated at the B3LYP/cc-PVDZ level.

E_0Q_0 (a.u)	E_+Q_+(a.u)	E_-Q_-(a.u)	E_0Q_+(a.u)	E_0Q_-(a.u)	E_+Q_0(a.u)	E_-Q_0(a.u)	IP (eV)	EA (eV)	λ_{hole} (eV)	λ_{ele} (eV)	λ_{int} (eV)
-2328.41	-2328.19	-2328.47	-2328.18	-2328.46	-2328.40	-2328.40	6.05	1.71	0.25	0.42	0.67
-2658.72	-2658.50	-2658.79	-2658.49	-2658.78	-2658.71	-2658.71	5.91	1.87	0.27	0.33	0.61
-2557.46	-2557.25	-2557.52	-2557.24	-2557.51	-2557.46	-2557.45	5.81	1.63	0.20	0.41	0.61
-2887.77	-2887.56	-2887.84	-2887.56	-2887.83	-2887.77	-2887.76	5.69	1.78	0.21	0.33	0.54
-3293.70	-3293.49	-3293.78	-3293.49	-3293.78	-3293.70	-3293.70	5.73	2.21	0.17	0.32	0.50
-3624.01	-3623.80	-3624.09	-3623.80	-3624.09	-3624.01	-3624.00	5.63	2.24	0.18	0.28	0.46
-3248.66	-3248.45	-3248.72	-3248.45	-3248.71	-3248.65	-3248.65	5.66	1.64	0.18	0.41	0.60
-3578.97	-3578.76	-3579.03	-3578.76	-3579.03	-3578.96	-3578.96	5.57	1.80	0.19	0.33	0.52
-3984.90	-3984.69	-3984.98	-3984.69	-3984.97	-3984.89	-3984.89	5.62	2.23	0.16	0.36	0.52
-4315.21	-4315.00	-4315.29	-4315.00	-4315.28	-4315.20	-4315.20	5.53	2.26	0.16	0.30	0.46

Table AS3 Calculated singlet excitation energies and oscillator strengths of ten dye-TiO_2 complexes

	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contributions
A1	1	16887.75	592.1451	2.1319	Singlet-A	HOMO->L+11 (17%), HOMO->L+12 (18%)
	2	18696.06	534.872	0.0318	Singlet-A	H-1->LUMO (11%), HOMO->LUMO (57%), HOMO->L+1 (11%)
	3	19830.89	504.2638	0.0428	Singlet-A	H-1->L+2 (11%), HOMO->L+2 (43%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
A1-F	1	16085.23	621.6885	2.7351	Singlet-A	HOMO->L+6 (28%)
	2	20076.89	498.0851	0.0065	Singlet-A	HOMO->LUMO (92%)
	3	20536.63	486.9348	0.0068	Singlet-A	HOMO->L+1 (77%), HOMO->L+2 (11%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
C218	1	16437.69	608.3579	2.251	Singlet-A	HOMO->L+7 (20%), HOMO->L+11 (17%)
	2	19430.84	514.6459	0.0099	Singlet-A	H-1->LUMO (11%), HOMO->LUMO (85%)
	3	19949.46	501.2668	0.0057	Singlet-A	H-1->L+1 (12%), HOMO->L+1 (58%), HOMO->L+2 (16%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
C218-F	1	15839.23	631.344	2.7023	Singlet-A	HOMO->L+7 (21%), HOMO->L+9 (11%)
	2	18790.43	532.1858	0.0041	Singlet-A	HOMO->LUMO (94%)
	3	19588.92	510.4926	0.011	Singlet-A	HOMO->L+1 (87%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
D2	1	8974.593	1114.257	0.0004	Singlet-A	H-3->L+6 (13%), H-1->L+6 (17%), HOMO->L+6 (65%)
	2	13371.96	747.8336	2.2653	Singlet-A	HOMO->L+2 (29%), HOMO->L+3 (14%), HOMO->L+4 (23%)
	3	18199.22	549.4741	0.0084	Singlet-A	H-1->L+6 (62%), HOMO->L+6 (15%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
D2-F	1	8460.814	1181.919	0.0004	Singlet-A	H-2->L+6 (13%), H-1->L+6 (10%), HOMO->L+6 (72%)

	2	12775.1	782.7725	2.9633	Singlet-A	HOMO->LUMO (29%), HOMO->L+1 (21%)
	3	17668.5	565.9789	0.429	Singlet-A	H-1->LUMO (12%), HOMO->L+10 (13%), HOMO->L+12 (14%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
Y123	1	16239.28	615.7909	2.4368	Singlet-A	HOMO->L+7 (16%), HOMO->L+10 (11%)
	2	19221.13	520.2607	0.0086	Singlet-A	H-1->LUMO (13%), HOMO->LUMO (83%)
	3	19796.21	505.1472	0.0132	Singlet-A	H-1->L+1 (13%), HOMO->L+1 (60%), HOMO->L+2 (12%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
Y123-F	1	15981.99	625.7044	2.7325	Singlet-A	HOMO->L+7 (22%), HOMO->L+9 (10%)
	2	18981.58	526.8264	0.0025	Singlet-A	HOMO->LUMO (92%)
	3	19747.82	506.3851	0.0107	Singlet-A	HOMO->L+1 (81%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
Y1234	1	8577.766	1165.805	0.0006	Singlet-A	H-1->L+4 (21%), HOMO->L+4 (51%)
	2	13430.84	744.5552	2.2745	Singlet-A	H-1->L+2 (18%), HOMO->L+2 (60%)
	3	17891.92	558.9115	0.0098	Singlet-A	H-3->L+4 (10%), H-1->L+4 (44%), HOMO->L+4 (15%)
	No.	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Symmetry**	**Major contributions**
Y1234-F	1	8370.48	1194.675	0.0017	Singlet-A	H-1->L+7 (16%), HOMO->L+7 (65%)
	2	13357.44	748.6464	2.687	Singlet-A	H-1->L+3 (10%), HOMO->L+2 (16%), HOMO->L+3 (37%)
	3	18115.34	552.0184	0.0032	Singlet-A	H-3->L+7 (11%), H-1->L+7 (57%), HOMO->L+7 (10%)

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According to the Jablonski diagram, there are three main decay pathways for S1: (i) the radiative decay from S1 to S0 with a rate k_r; (ii) the nonradiative internal conversion (IC) from S1 to S0 with a rate k_{IC}; (iii) the intersystem crossing (ISC) process from S1 to the first triplet excited state (T1) with a rate k_{ISC}. The rate constant for radiative transition (k_r) describes the electric dipolar coupling of the excited states with the ground states. Whereas, the radiationless transition (k_{IC}) describes the role of vibronic and spin orbit interactions.
The radiative decay rate, i.e., the spontaneous emission rate, is simply the integration of the light emission spectrum

$$k_r = \int_0^\infty \sigma_{em}(\omega) d\omega$$

According to Fermi's golden rule, the nonradiative internal conversion rate can be expressed as

$$k_{IC} = \frac{2\pi}{\mathrm{h}} |H'_{fi}| 2\delta(E_{fi} + E_{fv_f} - E_{iv_i})$$

Here the perturbation is the non-Born–Oppenheimer coupling. A detailed description is in a reference of [Peng et al., J. Chem. Phys. 134, 074510 (2011)]. However, this is not valid any more when the molecular level shifts closer to the conduction band edge. Therefore, we have considered the photo induced surface electron transfer process based on evidence from explicit electronic structure calculations. This approach allows the evaluation of the effects of the adsorption on the sensitizer electronic levels (generally only the dye LUMO is analyzed), characterizing them in terms of an energy shift relative to the free dye and a lifetime broadening, $\hbar\Gamma$. This lifetime broadening is well-described by a Lorentzian distribution resulting from the decay of the dye excited state, here approximated by the dye LUMO, coupled to the continuum of the TiO_2 CB states. To calculate these quantities we need to evaluate the projected density of states (PDOS) relative to the dye's LUMO in the complex.
When the system's molecular orbitals in a certain atomic basis are expanded, the contributions pi to the dye's LUMO PDOS are defined by the relation

$$p_i = \frac{\sum_j^n (c_{ij}^{\ A})^2}{\sum_j (c_{ij}^{\ A})^2}$$

where c_{ij}^{A} are the expansion coefficients of the complex molecular orbitals on the basis function of atom A belonging to the dye. The center of this distribution corresponds to the energy of the sensitizer's LUMO adsorbed on TiO_2, $E_{LUMO}(ads)$, and it can be calculated through the relation

$$E_{LUMO}(ads) = \sum_i p_i \varepsilon_i$$

On the other hand, the width of the LUMO broadening can be estimated as a mean deviation of a distribution centered at the E_{LUMO}(ads) energy value through the equation

$$\hbar\Gamma = \sum_i p_i \,|\, \varepsilon_i - E_{LUMO}(ads) \,|$$

The PDOS of the complex A1 obtained at the B3LYP/3-21G(d) level and estimated the width of the LUMO broadening using above procedure.

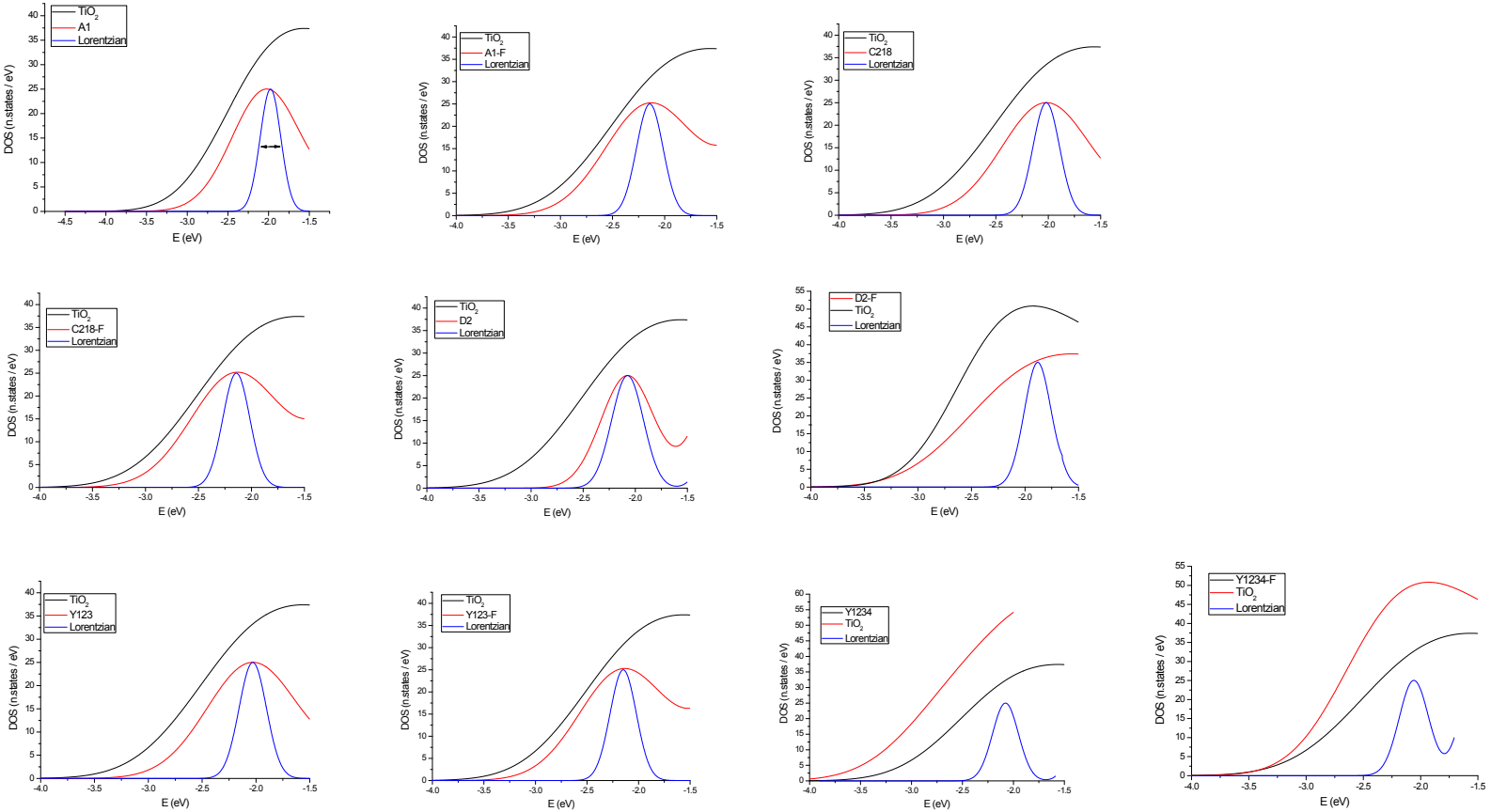

Fig: PDOS relative to the sensitizer and to TiO_2 and corresponding Lorentzian distribution of the dye's LUMO for A1. The TiO_2 PDOS have been normalized; those corresponding to the sensitizer have been normalized and multiplied by 50; and the Lorentzian distributions have been normalized on the dye's PDOS maximum.

The LUMO broadening gives a direct estimation of the electron transfer time that can be evaluated by $\tau(fs) = 658/\Gamma(meV)$.
The calculated results of all the systems were presented in Table 3.