Supporting Information

Anchoring Group Engineering in Coumarin-Benzothiazole Sensitizers: A First-Principles Perspective for DSSCs

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Table S1 : Coordinates of the designed dyes in the angstrom unit.

1. Dye A1

Atoms	Coordinates (Angstroms) X	Y	Z
C	-3.745186	-1.858724	0.229111
C	-5.112663	-1.697804	0.257370
C	-5.705254	-0.396326	0.272493
C	-4.833553	0.717062	0.235364
C	-2.867925	-0.752694	0.204242
C	-3.461139	0.527792	0.207797
C	-1.452965	-0.835159	0.166177
C	-0.667949	0.291504	0.136293
C	-1.293295	1.611806	0.143023
O	-2.683292	1.648646	0.178166
N	-7.070865	-0.233392	0.335298
C	-7.671882	1.103235	0.299465
C	-7.975100	-1.386258	0.355197
C	-8.264088	-2.004451	-1.019014
C	-7.772338	1.727720	-1.098445
C	0.786684	0.180526	0.095857
N	1.395596	-0.977514	0.085840
S	1.854715	1.605813	0.055487
C	2.760367	-0.826951	0.045107
C	3.222213	0.512053	0.022851
O	-0.714613	2.677479	0.120267
C	3.695910	-1.879150	0.024239
C	5.045008	-1.584899	-0.017304

C	5.514970	-0.244848	-0.039549
C	4.583214	0.805018	-0.019015
H	-8.924357	-2.871225	-0.909346
H	-7.344806	-2.336423	-1.509223
H	-8.756575	-1.285870	-1.680000
H	-8.415901	1.132579	-1.752361
H	-6.790673	1.806656	-1.572839
H	-8.197893	2.734224	-1.028941
H	-7.109130	1.763332	0.968356
H	-8.671560	1.017403	0.734698
H	-8.912100	-1.050260	0.808702
H	-7.571189	-2.144943	1.033645
H	-5.735621	-2.581466	0.263040
H	-3.324006	-2.860031	0.220441
H	-5.194661	1.735414	0.225675
H	-0.963337	-1.804656	0.159941
H	3.341278	-2.904284	0.040930
H	5.761245	-2.399366	-0.033569
H	4.931771	1.833512	-0.035846
C	6.934129	0.096386	-0.083424
C	7.981917	-0.751841	-0.106731
C	9.384857	-0.317908	-0.151344
O	10.336218	-1.077120	-0.171909
O	9.547150	1.035288	-0.168634
H	10.507212	1.176758	-0.197848
H	7.156624	1.160958	-0.098726
H	7.865841	-1.829853	-0.094149

2. Dye A2

C	-4.929305	-1.847351	0.014194
C	-6.289737	-1.638911	0.071936
C	-6.831211	-0.325990	0.235973
C	-5.917858	0.751362	0.308116
C	-4.010387	-0.779525	0.102897
C	-4.553543	0.514420	0.248034
C	-2.598876	-0.911433	0.050686
C	-1.770961	0.180241	0.138066
C	-2.345229	1.515957	0.282683
O	-3.733149	1.601695	0.330215

N	-8.189623	-0.120492	0.335727
C	-8.737001	1.229673	0.493328
C	-9.138138	-1.230111	0.212303
C	-9.437303	-1.666424	-1.228036
C	-8.859947	2.034233	-0.807378
C	-0.320346	0.016057	0.087636
N	0.242050	-1.156888	-0.034163
S	0.803882	1.396544	0.188124
C	1.614622	-1.057040	-0.057730
C	2.128285	0.258746	0.047211
O	-1.727066	2.556160	0.364967
C	2.508499	-2.134515	-0.171882
C	3.870863	-1.884991	-0.175884
C	4.389712	-0.570632	-0.071762
C	3.500371	0.506583	0.040015
H	-10.131934	-2.513102	-1.227511
H	-8.526935	-1.973599	-1.750081
H	-9.894414	-0.854226	-1.800070
H	-9.244564	3.036638	-0.592146
H	-9.547679	1.551839	-1.507674
H	-7.892638	2.141917	-1.305235
H	-8.124951	1.776472	1.218517
H	-9.724199	1.125400	0.952927
H	-10.065871	-0.913688	0.697576
H	-8.772075	-2.081248	0.796386
H	-6.946561	-2.493666	-0.010954
H	-4.547050	-2.857093	-0.105830
H	-6.239996	1.778045	0.406900
H	-2.146798	-1.892942	-0.058946
H	2.118482	-3.142757	-0.263722
H	4.561712	-2.713885	-0.291351
H	3.880064	1.517053	0.149830
C	5.853987	-0.336768	-0.080592
C	6.733964	-1.232790	0.554139
C	8.107257	-1.016206	0.550957
C	6.404681	0.789067	-0.721567
C	7.775474	1.011257	-0.725644
C	8.640570	0.110410	-0.090171
C	10.096525	0.392987	-0.125767
O	10.838490	-0.543641	0.521565

O	10.608341	1.353175	-0.668403
H	11.760672	-0.252545	0.430829
H	5.749810	1.479776	-1.243239
H	8.200606	1.874665	-1.225922
H	8.770580	-1.711507	1.052549
H	6.331897	-2.093541	1.078911

3. Dye A3

C	-4.126697	1.851015	-0.237855
C	-5.496383	1.717205	-0.263420
C	-6.114983	0.426933	-0.271030
C	-5.265336	-0.703971	-0.229871
C	-3.271316	0.727147	-0.208892
C	-3.890035	-0.542143	-0.205593
C	-1.856597	0.782263	-0.173290
C	-1.094046	-0.361161	-0.139933
C	-1.744795	-1.668613	-0.140561
O	-3.134685	-1.678228	-0.172475
N	-7.482191	0.290919	-0.330379
C	-8.109914	-1.033767	-0.285333
C	-8.364531	1.461289	-0.358706
C	-8.643421	2.092770	1.011359
C	-8.219549	-1.646821	1.116759
C	0.360421	-0.279679	-0.101941
N	0.993038	0.867708	-0.094993
S	1.397058	-1.726838	-0.060703
C	2.351997	0.690628	-0.056280
C	2.786766	-0.659605	-0.032642
O	-1.185699	-2.744760	-0.115159
C	3.308065	1.724283	-0.038627
C	4.652693	1.411741	0.001246
C	5.096558	0.059028	0.024786
C	4.138080	-0.976059	0.006942
H	-9.286661	2.971303	0.895029
H	-7.718928	2.410179	1.501388
H	-9.151026	1.388033	1.675756
H	-8.849474	-1.034686	1.768179
H	-7.238674	-1.742855	1.589625

H	-8.665678	-2.644777	1.054392
H	-7.561926	-1.708725	-0.951568
H	-9.108470	-0.930347	-0.718999
H	-9.306909	1.140127	-0.811595
H	-7.945220	2.207498	-1.041387
H	-6.101837	2.612855	-0.272467
H	-3.685384	2.843583	-0.234619
H	-5.646863	-1.714736	-0.214919
H	-1.347708	1.741811	-0.171783
H	2.973392	2.755835	-0.056514
H	5.377307	2.214804	0.014612
H	4.466208	-2.011186	0.024614
C	6.484543	-0.357162	0.066949
C	7.653331	0.349207	0.096399
C	8.971212	-0.339680	0.139022
O	10.041367	0.230125	0.167557
O	8.866627	-1.694274	0.143387
H	9.779662	-2.023594	0.172340
H	6.623575	-1.434315	0.077647
C	7.744375	1.776230	0.090737
N	7.808891	2.938403	0.085899

4. Dye A4

C	-6.288474	-1.684419	0.420391
C	-7.597858	-1.259210	0.431670
C	-7.927656	0.126465	0.299034
C	-6.859227	1.038019	0.128328
C	-5.215310	-0.779216	0.266834
C	-5.550186	0.584388	0.120361
C	-3.844848	-1.138011	0.243912
C	-2.857342	-0.195756	0.083523
C	-3.215955	1.211790	-0.074385
O	-4.572268	1.521252	-0.044082
N	-9.233535	0.556779	0.351370
C	-9.564262	1.978802	0.220408
C	-10.343978	-0.392385	0.470581
C	-10.742634	-1.085881	-0.838791

C	-9.624192	2.497892	-1.222059
C	-1.453771	-0.590821	0.069982
N	-1.086552	-1.842008	0.209067
S	-0.130046	0.579079	-0.130403
C	0.277410	-1.968567	0.167540
C	0.998219	-0.758872	-0.012323
O	-2.444052	2.133673	-0.229438
C	0.987309	-3.177453	0.288022
C	2.365141	-3.148926	0.226409
C	3.096655	-1.936867	0.043509
C	2.385664	-0.724747	-0.076150
H	-11.564755	-1.786050	-0.656918
H	-9.906757	-1.646626	-1.266033
H	-11.075403	-0.359083	-1.584890
H	-10.407431	1.991086	-1.792845
H	-8.675265	2.345469	-1.743269
H	-9.844572	3.570442	-1.224570
H	-8.844652	2.562928	0.803332
H	-10.533780	2.129605	0.704089
H	-11.199304	0.164733	0.862822
H	-10.098485	-1.138346	1.234178
H	-8.379557	-1.997517	0.544168
H	-6.067850	-2.742480	0.529361
H	-7.018649	2.098418	-0.004365
H	-3.551249	-2.177592	0.356642
H	0.443691	-4.105601	0.427299
H	2.917906	-4.079440	0.320127
H	2.924122	0.203135	-0.213732
C	4.540141	-2.079528	-0.000274
C	5.599572	-1.235420	-0.164511
C	5.663692	0.220830	-0.373975
O	4.751885	1.030185	-0.458441
S	7.260187	-1.895791	-0.145356
N	7.008727	0.630892	-0.506039
C	7.998690	-0.319461	-0.397487
S	9.627031	-0.069197	-0.502707
C	7.301245	2.042548	-0.619432
C	7.471079	2.689292	0.763020
O	7.262618	2.125966	1.802239
O	7.855439	3.988280	0.727800

H	8.010158	4.280463	-0.182622
H	8.214244	2.163396	-1.208760
H	6.456223	2.514812	-1.129138
H	4.842419	-3.118607	0.130325

5. Dye A5

C	7.765703	1.589028	-0.045899
C	9.083266	1.189742	-0.006105
C	9.435978	-0.179934	0.205336
C	8.380207	-1.110455	0.346980
C	6.706303	0.668778	0.108544
C	7.062769	-0.682517	0.303239
C	5.327602	0.999115	0.072481
C	4.354693	0.041985	0.224009
C	4.735849	-1.353653	0.427591
O	6.098029	-1.635579	0.453464
N	10.752859	-0.574638	0.283157
C	11.106549	-1.985089	0.467335
C	11.846117	0.384365	0.105131
C	12.181443	0.716155	-1.354889
C	11.059218	-2.835159	-0.809241
C	2.941855	0.408602	0.181605
N	2.550072	1.642448	0.000825
S	1.635251	-0.789677	0.368803
C	1.177926	1.738260	-0.004708
C	0.483800	0.516481	0.177850
O	3.977607	-2.288353	0.575676
C	0.445035	2.925074	-0.169487
C	-0.938690	2.873746	-0.144690
C	-1.637161	1.654310	0.036839
C	-0.908988	0.467652	0.199999
H	12.983881	1.460241	-1.396594
H	11.313157	1.121344	-1.881613
H	12.516815	-0.173369	-1.895347
H	11.781735	-2.479153	-1.549018
H	10.067499	-2.812785	-1.268682
H	11.300952	-3.876885	-0.573957
H	10.452840	-2.417005	1.232679

H	12.116332	-2.010689	0.886842
H	12.727426	-0.039790	0.594824
H	11.610940	1.300647	0.656751
H	9.852914	1.936957	-0.141656
H	7.528437	2.637165	-0.204750
H	8.554673	-2.167162	0.490220
H	5.017809	2.029215	-0.077896
H	0.972977	3.860683	-0.320794
H	-1.504140	3.787141	-0.299108
H	-1.427264	-0.470073	0.370933
C	-3.119143	1.632798	0.053836
C	-3.847086	2.714066	0.636041
C	-5.220670	2.717714	0.672683
C	-5.955516	1.633025	0.129847
C	-5.241545	0.548419	-0.462323
C	-3.830551	0.571277	-0.490565
C	-7.364805	1.549985	0.143770
C	-8.021426	0.440113	-0.359886
C	-7.188890	-0.549428	-0.988472
N	-5.895996	-0.504222	-1.041033
C	-9.487305	0.401388	-0.280113
C	-10.289482	-0.562422	0.234864
C	-11.710541	-0.394243	0.168307
C	-9.781884	-1.782760	0.970186
N	-12.874291	-0.339317	0.144567
O	-8.628116	-1.914433	1.293872
O	-10.705191	-2.713462	1.287775
H	-11.587390	-2.470756	0.963196
C	-7.947274	-1.875554	-1.868571
H	-3.297751	3.535106	1.084568
H	-5.755902	3.543111	1.134158
H	-7.940070	2.355834	0.593178
H	-9.990933	1.291335	-0.654933
H	-3.326223	-0.255656	-0.977621

6. Dye A6

C	7.524012	1.527066	-0.659577
C	8.853394	1.172720	-0.600484

C	9.262471	-0.078522	-0.041457
C	8.247841	-0.946357	0.425977
C	6.506154	0.672585	-0.182602
C	6.917467	-0.565355	0.355932
C	5.118568	0.962089	-0.211922
C	4.188652	0.073268	0.269638
C	4.626435	-1.205110	0.824482
O	5.995017	-1.451462	0.831359
N	10.593241	-0.417773	0.051598
C	11.004729	-1.706780	0.615271
C	11.640973	0.458037	-0.480609
C	11.846611	0.369948	-1.998556
C	10.926546	-2.891589	-0.356494
C	2.765534	0.395676	0.231848
N	2.319850	1.524038	-0.254473
S	1.516452	-0.719558	0.845614
C	0.948322	1.596768	-0.180520
C	0.311148	0.466041	0.387993
O	3.908713	-2.070988	1.278833
C	0.165244	2.680381	-0.611687
C	-1.210787	2.620534	-0.467131
C	-1.852571	1.491265	0.099212
C	-1.074111	0.407359	0.529032
H	12.623632	1.074605	-2.313163
H	10.928701	0.611144	-2.541505
H	12.159639	-0.634160	-2.297753
H	11.599569	-2.750849	-1.206917
H	9.913706	-3.024159	-0.746119
H	11.217198	-3.814891	0.155379
H	10.403904	-1.910159	1.507891
H	12.033664	-1.589922	0.967591
H	12.570665	0.190227	0.029202
H	11.427318	1.491407	-0.187241
H	9.589098	1.863366	-0.988700
H	7.243977	2.486126	-1.086015
H	8.464682	-1.919446	0.842672
H	4.767079	1.905032	-0.620657
H	0.648829	3.542919	-1.057858
H	-1.817486	3.445739	-0.825473
H	-1.545107	-0.451056	0.996690

C	-3.327220	1.457854	0.237028
C	-4.048079	2.634245	0.563830
C	-5.420902	2.606038	0.702831
C	-6.146086	1.408967	0.524443
C	-5.426726	0.231420	0.198528
C	-4.034158	0.266301	0.053572
C	-7.565270	1.318979	0.640100
C	-8.259964	0.159519	0.406892
C	-7.520251	-1.096921	0.144713
N	-6.140345	-0.935889	0.032682
C	-9.708726	0.144710	0.528971
C	-10.598566	-0.619120	-0.156063
C	-11.979129	-0.589046	0.217320
C	-10.252260	-1.429014	-1.386719
N	-13.109910	-0.627424	0.497727
O	-9.414888	-1.079227	-2.179304
O	-11.004442	-2.528480	-1.602838
H	-11.603805	-2.692428	-0.858738
H	-3.507476	3.558284	0.735484
H	-5.962639	3.511810	0.960653
H	-8.114108	2.224886	0.889756
H	-10.122195	0.823526	1.272491
H	-3.507610	-0.639156	-0.232207
H	-5.646667	-1.798807	-0.161626
O	-8.014829	-2.214282	0.072058

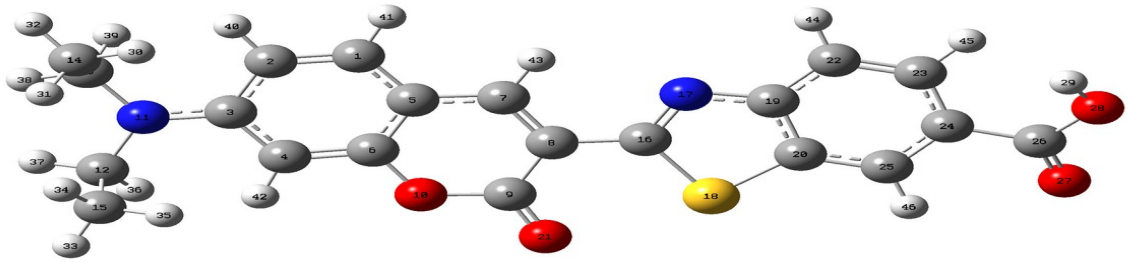

Fig. S1: Optimized structure of the test compound.

Table S2: Energies of HOMO, LUMO, Δ_{H-L}, and λ_{max} values of the test compound with different functional.

Functional	**HOMO (eV)**	**LUMO (eV)**	**Δ_{H-L} (eV)**	**λ_{max} (nm)**
Experimental	-5.45	-2.31	3.14	437
B3LYP	-5.60	-2.33	3.28	400
B3LYP-D3	-5.57	-2.30	3.27	403
B3PW91	-5.70	-2.41	3.29	417
CAM-B3LYP	-6.82	-1.16	5.65	455
PBEPBE	-4.96	-2.89	2.06	355
WB97XD	-7.39	-0.64	6.74	358

Table S3: Validation of basis set.

Compound	**6-311G (d,p)**	**6-31G (d,p)**	**reported value**
C6N	457 nm	455 nm	437 nm

We have also validated the basis sets used in our calculations. To further evaluate the reliability of the employed basis sets, we conducted additional test calculations using the reference compound C6N with both double-zeta and triple-zeta basis sets (6-31G (d,p)

and 6-311G (d,p), respectively) with CAM-B3LYP functional. The results of these tests have presented in Table S3. From this Table, it is evident that the double-zeta basis set shows a closer match with the reported results, affirming its appropriateness for our calculations. We are confident that this selected basis set offers a reasonable compromise between computational cost and accuracy for the systems under investigation.

To provide the necessary validation for chosing Ti_5O_{10} cluster, we have carried out literature survey and selected one publication where Ti_9O_{18} cluster has been used throughout their work (Phys. Chem. Chem. Phys., 2012, 14, 225–233). In this regard, we have chosen one of their reported dye (viz., NKX-2753) and anchored the same with our used Ti_5O_{10} cluster (in our manuscript) and carried out the optimization employing the same level of theory. The optimized structure of our designed NKX-2753-Ti_5O_{10} dye-cluster is presented in Fig. S2.

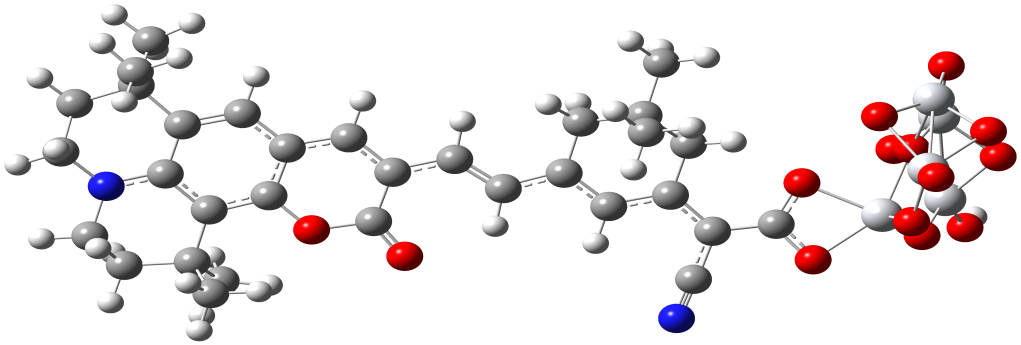

Fig. S2: Optimized structure of the NKX-2753-Ti_5O_{10} dye-cluster.

Here, our aim is to compare the calculated energy band gap (Δ_{H-L}) values of both the reported dye-cluster (NKX-2753-Ti_9O_{18}) and our designed NKX-2753-Ti_5O_{10} cluster. The respective Δ_{H-L} values of both the dye-clusters are reported in the Table S4:

Table S4: Validation of basis set.

Dye-cluster	Δ_{H-L} (eV)
NKX-2753-Ti_9O_{18}	1.319
NKX-2753- Ti_5O_{10}	1.317

From Table S4, it is evident that both the dye-clusters exhibit nearly the same Δ_{H-L} value. Hence, we can conclude that our used Ti_5O_{10} cluster is sufficient for the DFT and TD-DFT simulations.

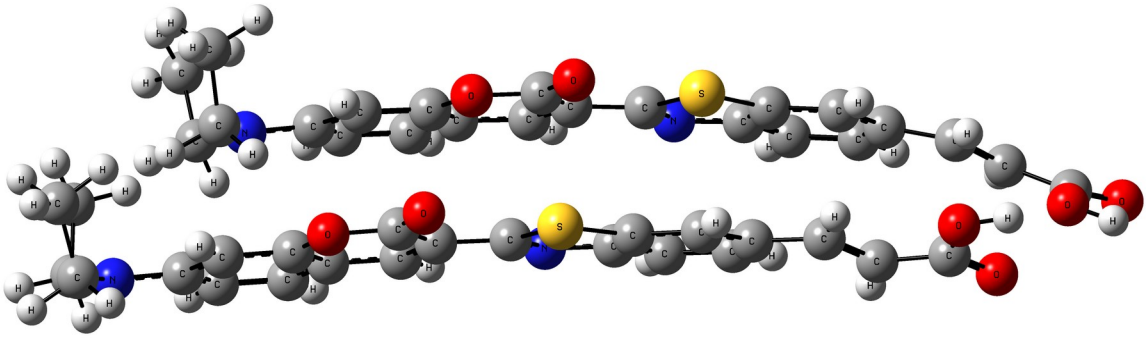

Fig. S3: Representative structure of two stacked dyes.

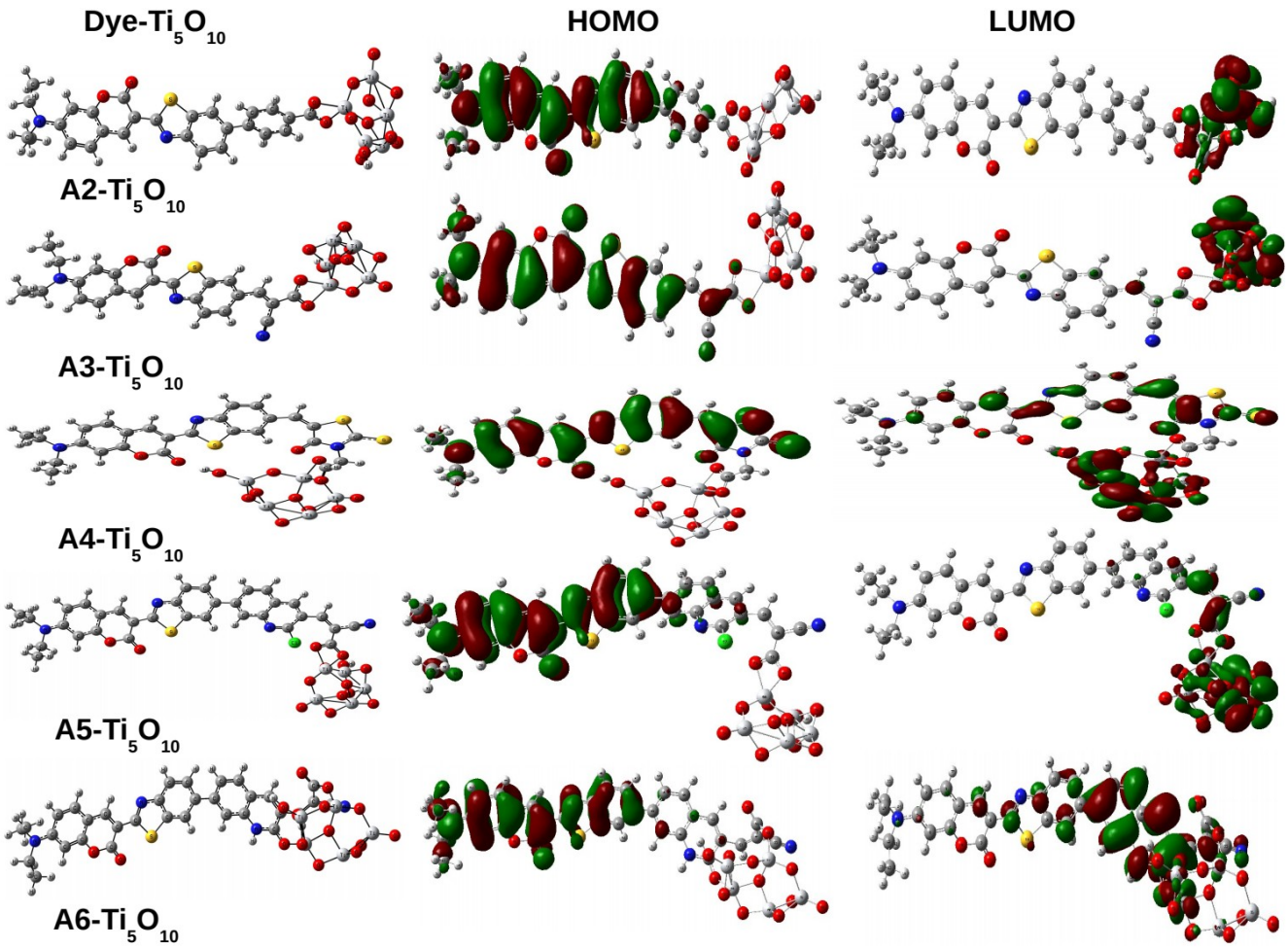

Fig. S4 : Optimized geometries of the dye-Ti_5O_{10} cluster along with their frontier molecular orbitals.