Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material

Theoretical Study on the Light Harvesting Efficiency of Zinc Porphyrin Sensitizers for DSSCs

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Table S1: Calculated singlet excitation energies and oscillator strengths of JC1 – 6 and YD2-o-C8 dyes.

Molecule	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
	1	16107.003	620.84796	0.2985	Singlet-A	H-1->L+1 (24%), HOMO->LUMO (70%)
	2	16827.261	594.27377	0.0061	Singlet-A	H-1->LUMO (53%), HOMO->L+1 (40%)
	3	21504.503	465.01889	0.3637	Singlet-A	H-2->LUMO (49%), H-1->L+1 (25%), HOMO->LUMO (17%)
YD2-o-C8	4	23495.093	425.62079	1.0563	Singlet-A	H-1->LUMO (40%), HOMO->L+1 (59%)
	5	23850.786	419.2734	1.8612	Singlet-A	H-2->LUMO (36%), H-1->L+1 (45%)
	6	26642.29	375.34311	0.3161	Singlet-A	H-2->L+1 (90%)
	7	29832.235	335.20787	0.017	Singlet-A	H-13->LUMO (14%), H-12->LUMO (39%), H-5->LUMO (11%), HOMO->L+2 (13%)
	8	30175.023	331.39992	0.0099	Singlet-A	H-14->LUMO (11%), H-12->LUMO (16%), H-5->LUMO (12%), HOMO->L+2 (30%)
	9	30811.399	324.55521	0.0284	Singlet-A	H-11->LUMO (48%), H-7->LUMO (17%)
	10	31304.207	319.44588	0.0402	Singlet-A	H-14->LUMO (25%), H-11->L+1 (13%), H-5->LUMO (19%), HOMO->L+2 (18%)

	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
	1	16589.326	602.79724	0.2727	Singlet-A	H-1->L+1 (29%), HOMO->LUMO (67%)
	2	17053.905	586.37598	0.004	Singlet-A	H-1->LUMO (53%), HOMO->L+1 (43%)
	3	23391.853	427.49926	2.3931	Singlet-A	H-1->L+1 (65%), HOMO->LUMO (30%)
	4	24271.81	412.00059	1.376	Singlet-A	H-1->LUMO (45%), HOMO->L+1 (54%)
JC1	5	26775.372	373.47753	0.0108	Singlet-A	H-2->LUMO (81%)
	6	29942.733	333.97085	0.0123	Singlet-A	H-11->LUMO (24%), H-6->LUMO (13%), H-2->L+1 (16%), HOMO->L+2 (23%)
	7	30006.452	333.26166	0.0042	Singlet-A	H-11->LUMO (10%), H-2->L+1 (62%)
	8	30205.672	331.06365	0.0019	Singlet-A	H-11->LUMO (54%), HOMO->L+2 (17%)
	9	30965.452	322.94055	0.0348	Singlet-A	H-12->L+1 (12%), H-10->LUMO (40%), H-7->LUMO (13%), H-2->L+1 (10%)
	10	31363.892	318.83798	0.0286	Singlet-A	H-12->LUMO (11%), H-11->L+1 (45%), H-10->L+1 (10%)
	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
	1	16458.663	607.58275	0.3294	Singlet-A	H-1->L+1 (27%), HOMO->LUMO (67%)
	2	17005.511	588.04466	0.0046	Singlet-A	H-1->LUMO (52%), HOMO->L+1 (42%)
	3	22801.451	438.56858	2.3421	Singlet-A	H-1->L+1 (59%), HOMO->LUMO (27%)
	4	24158.085	413.94009	1.3302	Singlet-A	H-1->LUMO (44%), HOMO->L+1 (54%)
JC2	5	26389.03	378.94534	0.0199	Singlet-A	H-2->LUMO (61%), HOMO->L+2 (14%)
	6	27975.534	357.4552	0.0122	Singlet-A	H-3->LUMO (10%), H-2->LUMO (22%), H-1->L+1 (11%), HOMO->L+2 (40%)
	7	29970.963	333.65628	0.0012	Singlet-A	H-2->L+1 (73%)
	8	30016.13	333.1542	0.005	Singlet-A	H-12->LUMO (46%), H-3->LUMO (25%), HOMO->L+2 (13%)
	9	30154.859	331.62152	0.003	Singlet-A	H-12->LUMO (39%), H-3->LUMO (31%), HOMO->L+2 (12%)
	10	30858.986	324.05472	0.0196	Singlet-A	H-11->LUMO (37%), H-9->L+1 (10%), H-7->LUMO (17%), H-2->L+1 (12%)
	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs

	1	16311.869	613.05052	0.4262	Singlet-A	H-1->L+1 (23%), HOMO->LUMO (68%)
	2	17035.354	587.01452	0.0045	Singlet-A	H-1->LUMO (48%), HOMO->L+1 (40%)
	3	21297.217	469.54492	1.3907	Singlet-A	H-3->LUMO (16%), H-1->L+1 (35%), HOMO->LUMO (17%), HOMO->L+2 (19%)
	4	24093.56	415.04866	1.2147	Singlet-A	H-1->LUMO (44%), HOMO->L+1 (53%)
JC3	5	24863.019	402.20378	0.7138	Singlet-A	H-3->LUMO (18%), H-2->LUMO (15%), H-1->L+1 (33%), HOMO->LUMO (10%), HOMO->L+2 (14%)
	6	26751.982	373.80408	0.0436	Singlet-A	H-3->LUMO (14%), H-2->LUMO (22%), HOMO->L+2 (48%)
	7	26945.556	371.1187	0.0043	Singlet-A	H-3->LUMO (29%), H-2->LUMO (40%)
	8	29603.978	337.79244	0.1086	Singlet-A	H-2->L+1 (11%), H-1->L+2 (75%)
	9	29937.894	334.02483	0.006	Singlet-A	H-2->L+1 (68%), H-1->L+2 (11%)
	10	29969.35	333.67424	0.0182	Singlet-A	H-13->LUMO (50%), H-13->L+2 (10%), H-3->L+2 (18%)
	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
	1	16021.508	624.16098	0.4232	Singlet-A	H-1->L+1 (17%), HOMO->LUMO (75%)
	2	17215.217	580.88145	0.0008	Singlet-A	H-1->LUMO (43%), HOMO->L+1 (47%)
	3	20919.747	478.01726	0.0955	Singlet-A	H-2->LUMO (60%), H-1->L+1 (17%), HOMO->LUMO (11%)
	4	23514.45	425.27041	0.8064	Singlet-A	H-1->LUMO (40%), HOMO->L+1 (52%)
	5	24397.633	409.87582	2.0609	Singlet-A	H-2->LUMO (23%), H-1->L+1 (57%)
JC4	6	26244.656	381.02995	0.6258	Singlet-A	H-2->L+1 (81%), H-1->LUMO (13%)
	7	30032.262	332.97526	0.0107	Singlet-A	H-2->L+2 (12%), HOMO->L+2 (54%)
	8	31201.774	320.4946	0.0319	Singlet-A	H-11->L+1 (11%), H-10->LUMO (46%), H-7->LUMO (14%)
	9	31653.447	315.92136	0.0105	Singlet-A	H-11->LUMO (25%), H-10->L+1 (12%), H-6->LUMO (31%), HOMO->L+2 (10%)
	10	31981.717	312.67865	0.0648	Singlet-A	H-9->LUMO (47%), H-3->LUMO (11%), H-3->L+1 (14%)
	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
	1	15890.845	629.29315	0.495	Singlet-A	H-1->L+1 (15%), HOMO->LUMO (74%)
	2	17215.217	580.88145	0.0003	Singlet-A	H-1->LUMO (42%), HOMO->L+1 (46%)

	3	20772.146	481.4139	0.063	Singlet-A	H-2->LUMO (60%), H-1->L+1 (15%)
	4	23490.253	425.70848	0.809	Singlet-A	H-1->LUMO (39%), HOMO->L+1 (53%)
JC5	5	23620.11	423.36806	2.0018	Singlet-A	H-2->LUMO (18%), H-1->L+1 (49%), HOMO->L+2 (11%)
	6	26180.938	381.95729	0.5492	Singlet-A	H-2->L+1 (82%), H-1->LUMO (12%)
	7	27969.081	357.53767	0.0578	Singlet-A	H-2->L+2 (15%), H-1->L+1 (17%), HOMO->L+2 (49%)
	8	29980.642	333.54856	0.0169	Singlet-A	H-3->LUMO (65%), HOMO->L+2 (16%)
	9	31142.088	321.10885	0.032	Singlet-A	H-11->LUMO (42%), H-10->L+1 (16%), H-7->LUMO (17%)
	10	31661.513	315.84088	0.0368	Singlet-A	H-11->L+1 (11%), H-10->LUMO (44%)
	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
	1	15715.822	636.30145	0.5535	Singlet-A	HOMO->LUMO (73%)
	2	17145.852	583.23143	0.0011	Singlet-A	H-2->LUMO (21%), H-1->LUMO (18%), HOMO->L+1 (48%)
	3	20822.96	480.23913	0.0152	Singlet-A	H-2->LUMO (29%), H-1->LUMO (35%)
	4	21890.845	456.81197	1.315	Singlet-A	H-3->LUMO (16%), H-2->L+1 (18%), H-1->L+1 (16%), HOMO->L+2 (17%)
JC6	5	23366.043	427.97148	0.7885	Singlet-A	H-2->LUMO (22%), H-1->LUMO (18%), HOMO->L+1 (50%)
	6	26039.79	384.02768	0.4715	Singlet-A	H-3->LUMO (10%), H-1->L+1 (58%)
	7	26106.734	383.04293	0.4283	Singlet-A	H-3->LUMO (31%), H-2->L+1 (43%)
	8	26493.883	377.44562	0.1696	Singlet-A	H-3->LUMO (18%), HOMO->L+2 (54%)
	9	30337.948	329.62019	0.1193	Singlet-A	H-2->L+2 (47%), H-1->L+2 (38%)
	10	30472.643	328.16319	0.0532	Singlet-A	H-3->LUMO (16%), H-3->L+2 (44%)

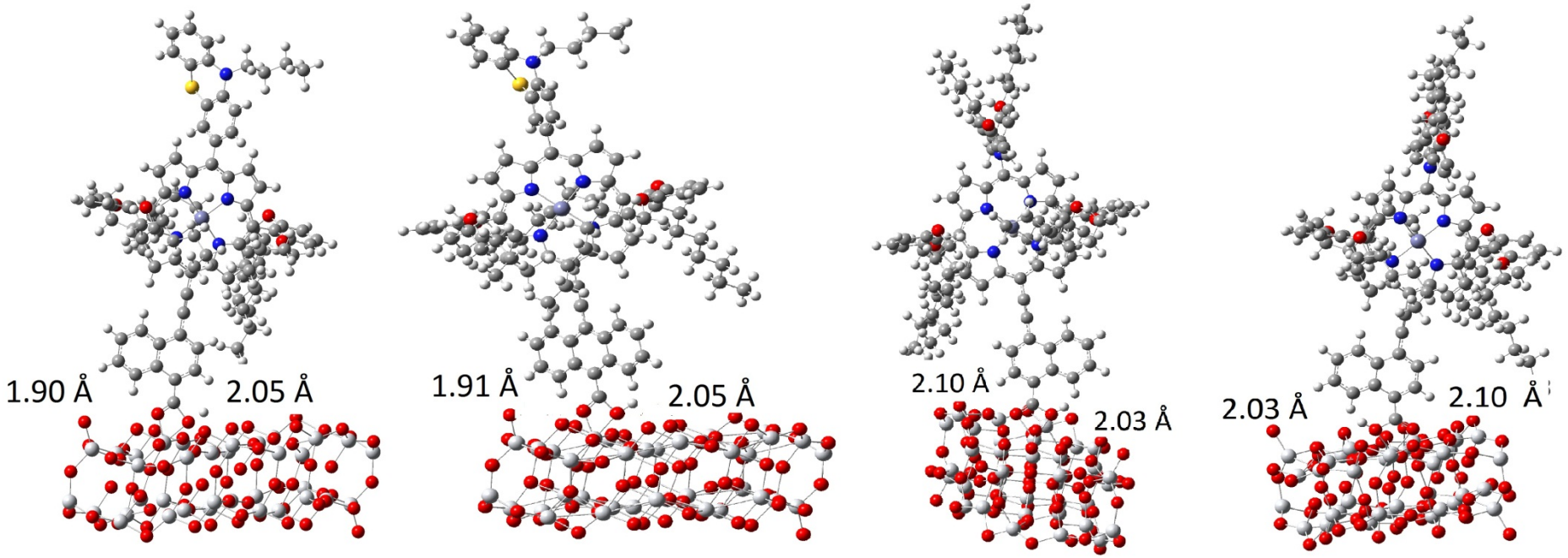

Figure S1. Optimized bidentate chelate bridging mode of JC2, JC3, JC5 and JC6 dyes on the $(TiO_2)_{36}$ cluster calculated by PBE/DNP on DMol3 program.

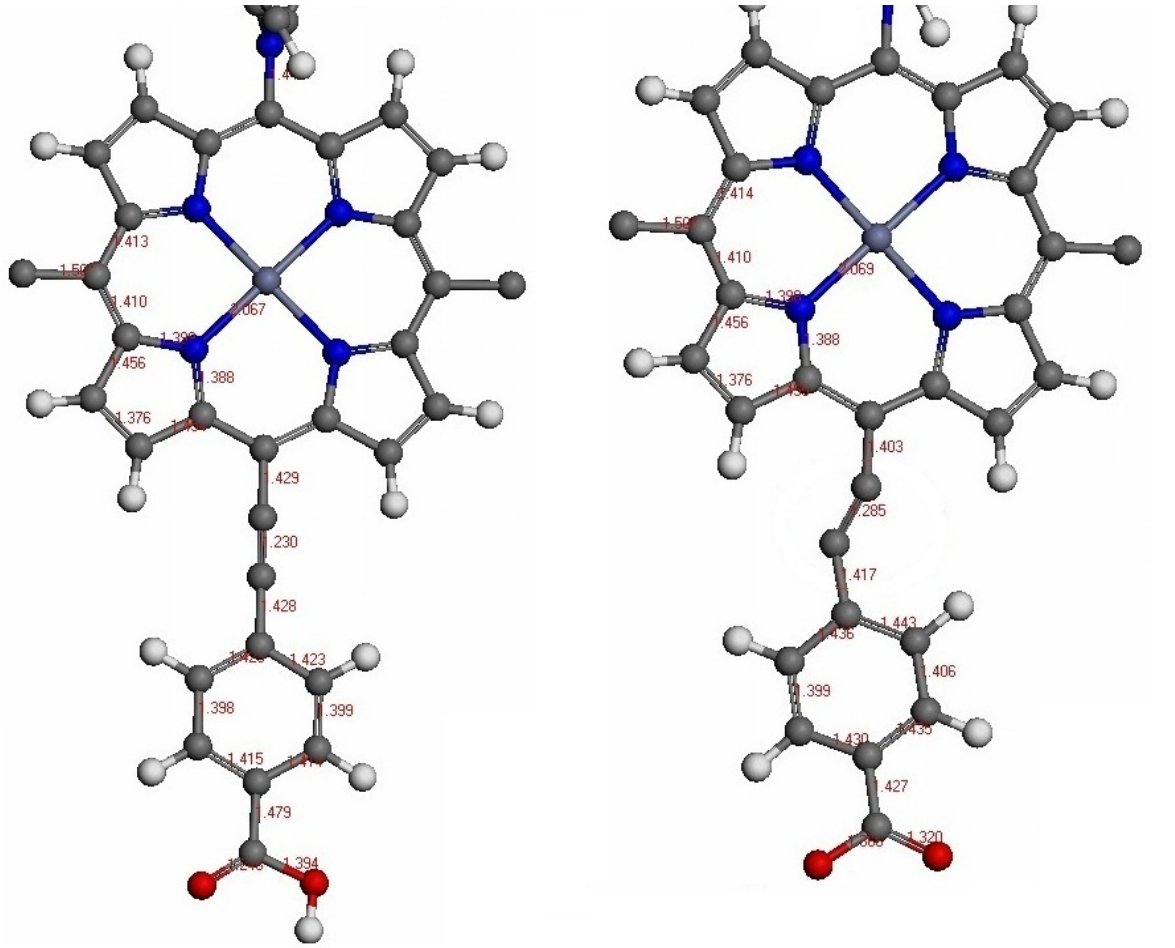

Figure S2: optimized geometry structures of YD2-o-C8 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6228.33 a.u, $E_{dy}e+TiO_2$ = -42196.3 a.u) calculated at GGA/PBE/DNP level using Dmol[3]

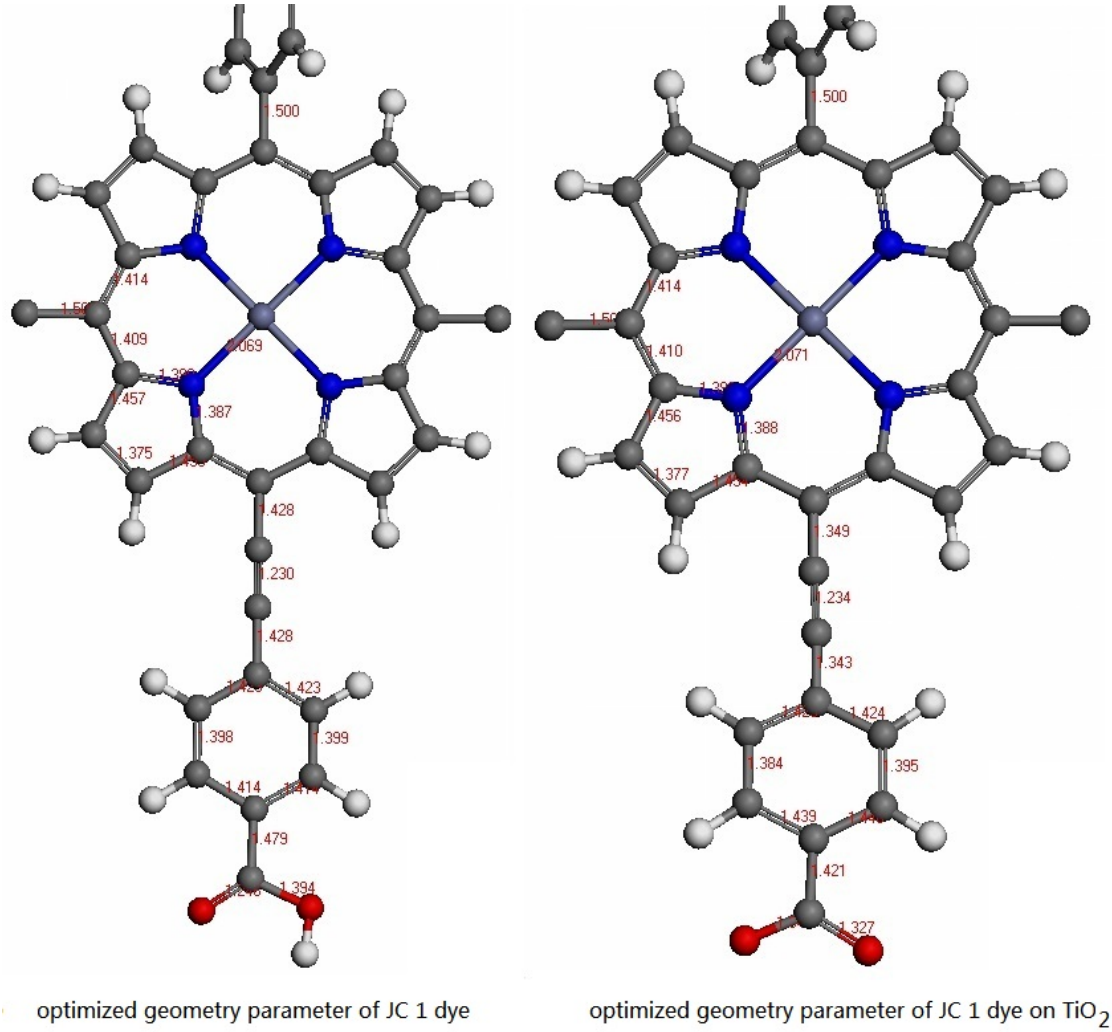

Figure S3: optimized geometry structures of JC1 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6314.93 a.u, $E_{dy}e+TiO_2$ = -42196.3 a.u) calculated at GGA/PBE/DNP level using $Dmol^3$

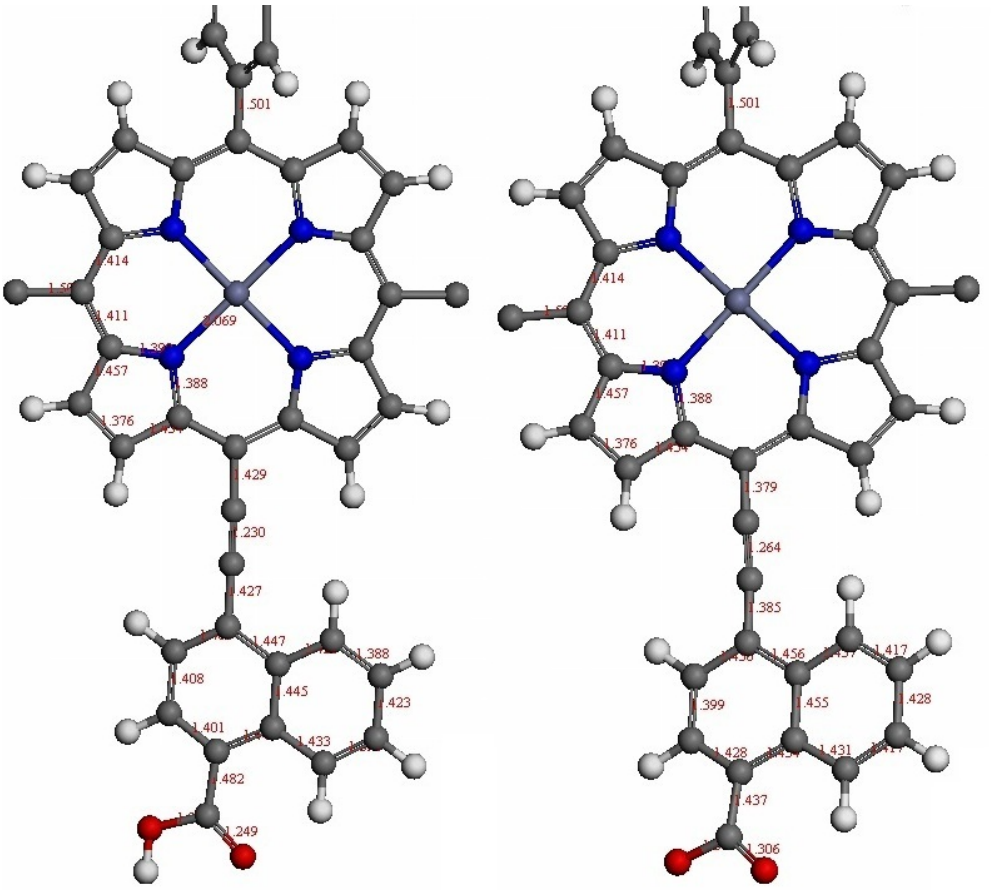

Figure S4: optimized geometry structures of JC2 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6467.1 a.u, $E_{dy}e+TiO_2$ = -42435.1 a.u) calculated at GGA/PBE/DNP level using Dmol^3

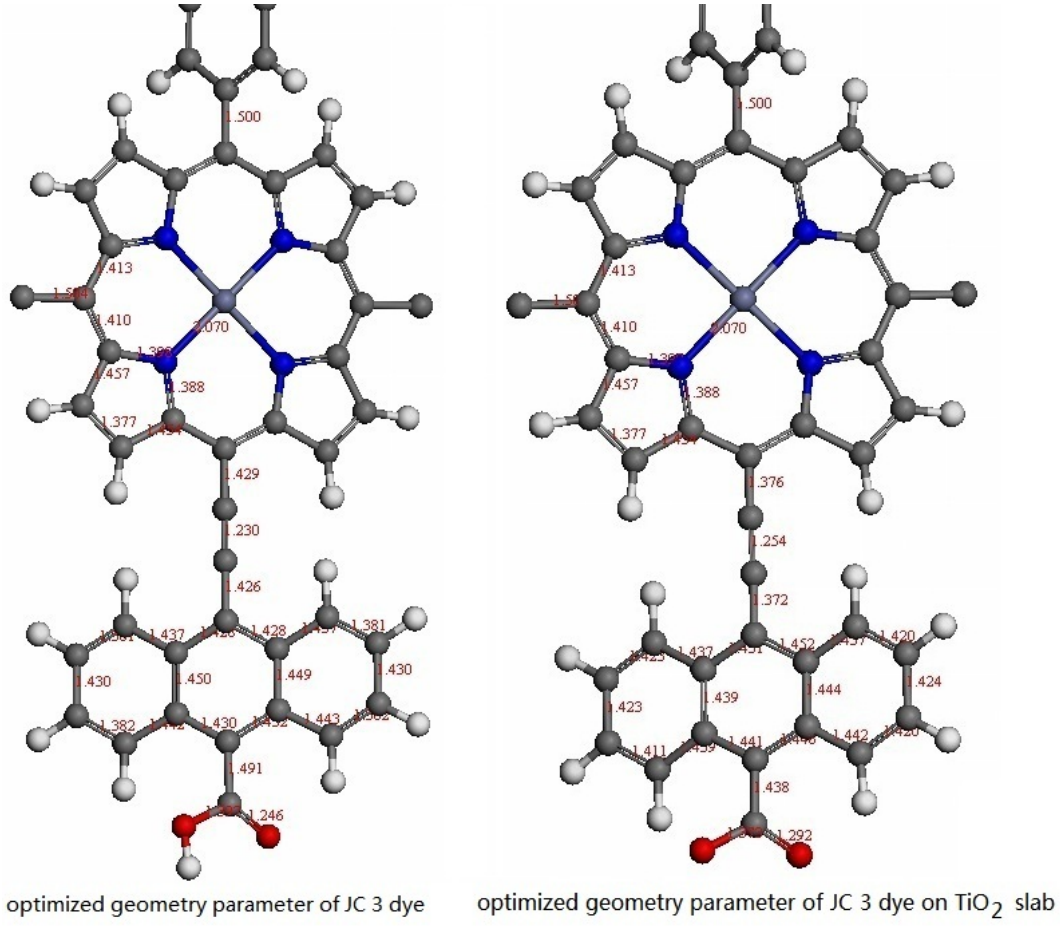

Figure S5: optimized geometry structures of JC3 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6619.27 a.u, $E_{dy}e+TiO_2$ = -42587.2 a.u) calculated at GGA/PBE/DNP level using Dmol[3]

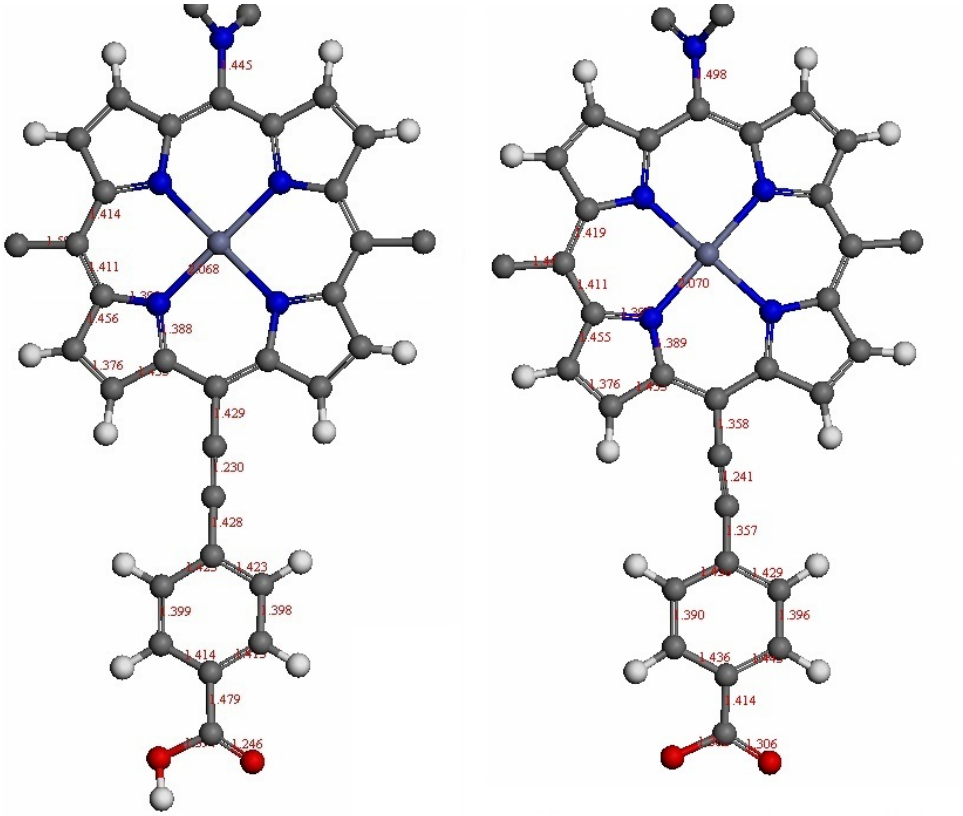

Figure S6: optimized geometry structures of JC4 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6378.33 a.u, $E_{dy}e+TiO_2$ = -42346.3a.u) calculated at GGA/PBE/DNP level using Dmol^3

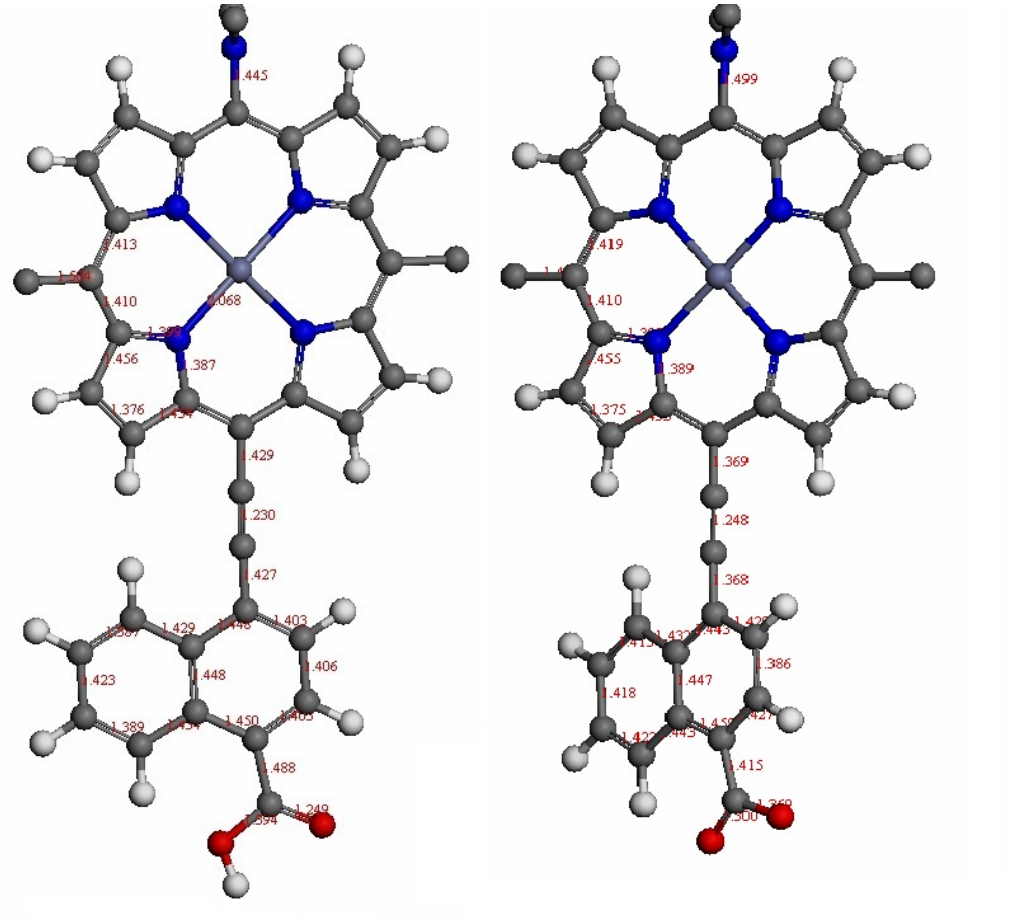

Figure S7: optimized geometry structures of JC5 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6530.5 a.u, $E_{dy}e+TiO_2$ = -42498.5 a.u) calculated at GGA/PBE/DNP level using Dmol^3

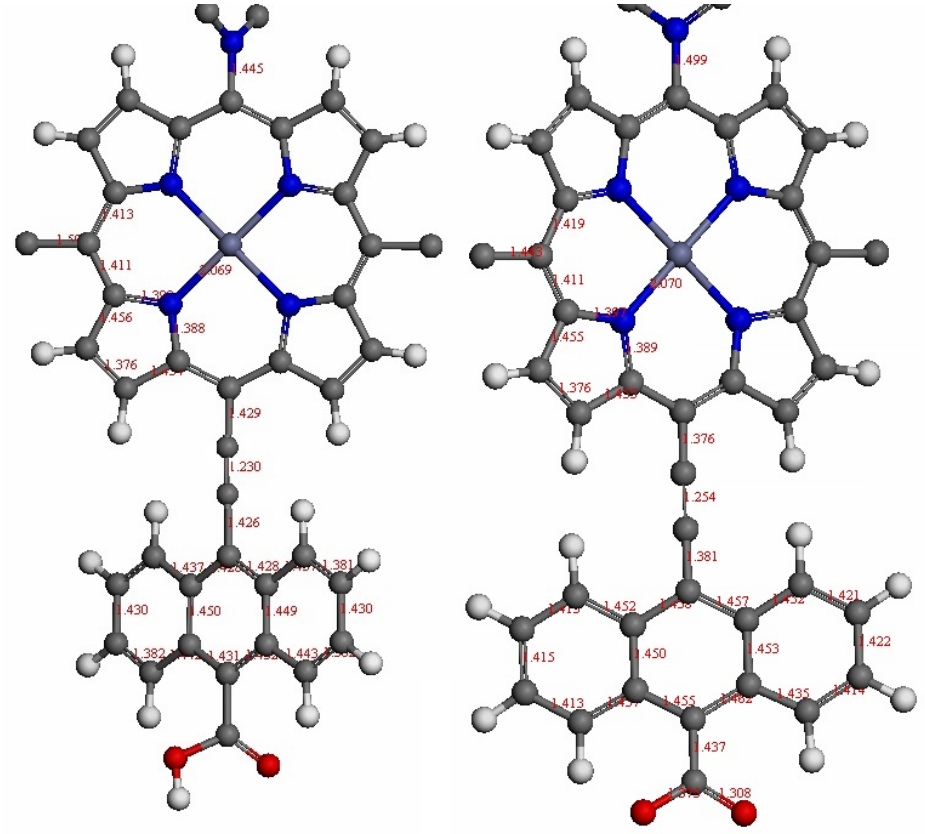

Figure S8: optimized geometry structures of JC6 dye before and after adsorption of dye on TiO2 surface (E_{dye} = -6682.68 a.u, $E_{dy}e+TiO_2$ = -42650.7 a.u) calculated at GGA/PBE/DNP level using Dmol[3]

Other supporting material

Table S2. The reorganization energies of the dyes JC1 – 6 calculated at the B3LYP/LanL2dZ level of theory.

Molecule	E0 g0	E- g-	E+ g+	E- g0	E+ g0	E0 g-	E0 g+	hole (a.u)	electron (a.u)	hole (eV)	electron (eV)
reference	-4559.283369	-4559.355387	-4559.077825	-4559.279311	-4559.279703	-4559.349706	-4559.07385	0.00764052	0.00973932	0.207909215	0.265020493
JC1	-4253.709953	-4253.781616	-4253.510797	-4253.705758	-4253.717701	-4253.777567	-4253.494257	0.00879124	0.00824302	0.239221913	0.224304081
JC2	-4407.325646	-4407.402038	-4407.124497	-4407.324712	-4407.329867	-4407.39471	-4407.111331	0.00894416	0.00826071	0.24338308	0.224785451
JC3	-4560.927962	-4561.005538	-4560.736615	-4560.922696	-4560.937692	-4560.998809	-4560.714949	0.01193566	0.01199543	0.324785971	0.326412396
JC4	-4709.686221	-4709.757129	-4709.485516	-4709.682188	-4709.481024	-4709.752454	-4709.682367	0.008347	0.00870875	0.227133522	0.236977245
JC5	-4863.298624	-4863.372842	-4863.097964	-4863.294405	-4863.093942	-4863.368056	-4863.294631	0.0080152	0.0090061	0.218104781	0.245068554
JC6	-5016.904667	-5016.980915	-5016.705088	-5016.898794	-5016.701172	-5016.975085	-5016.900808	0.0077754	0.01170251	0.211579488	0.318441634

Table S3. The adsorption energies of the dyes JC1 – 6 calculated at the PBE/DNP level of theory using Dmol[3] program.

Molecule	E_{TiO2} (a.u)	E_{dye} (a.u)	$E_{dye+TiO2}$ (a.u)	E_{ads} (a.u)	E_{ads} (kcal/mol)
reference	-35968	-6228.33	-42196.3	-0.02244	-14.1387
JC1	-35968	-6314.93	-42282.9	-0.02071	-13.0459
JC2	-35968	-6467.1	-42435.1	-0.02146	-13.5197
JC3	-35968	-6619.27	-42587.2	-0.02221	-13.9935
JC4	-35968	-6378.33	-42346.3	-0.0225	-14.1742
JC5	-35968	-6530.5	-42498.5	-0.02325	-14.6481
JC6	-35968	-6682.68	-42650.7	-0.024	-15.1219

Table S4. The first hyperpolarizability components of all the dyes JC1 - 6 calculated at the B3LYP/Lanl2dz level of theory

Component	YD2-o-C8	JC1	JC2	JC3	JC4	JC5	JC6
β_{xxx}	20036.3	67405	77692.28	74674	14414.7	15844.9	13506.3
β_{xxy}	-1044	-9977	-9846.118	-6955.5	-470.56	-955.55	-635.362
β_{xyy}	-182.94	1938.8	1736.132	1152.6	126.979	148.387	99.7056
β_{yyy}	202.882	-641.7	-570.7503	-406.23	241.675	266.402	250.643
β_{xxz}	-20344	-9686	-8135.176	-6704	-15722	-17499	-15139.9
β_{xyz}	877.822	689.98	243.8179	-107.98	458.256	1057.69	785.251
β_{yyz}	316.042	4.9522	117.7111	71.338	-12.126	-118.83	-18.6377
β_{xzz}	19612.6	859.47	294.2183	-122.99	15971.2	17916.6	15559.2
β_{yzz}	-605.45	-30.69	73.15644	19.089	-596.51	-1204.5	-1035.4
β_{zzz}	-17723	-64.8	132.8291	-2.094	-14361	-16398	-14026.9
B_{total}	54633	71672	80776.59	76348	42866	48069	41285

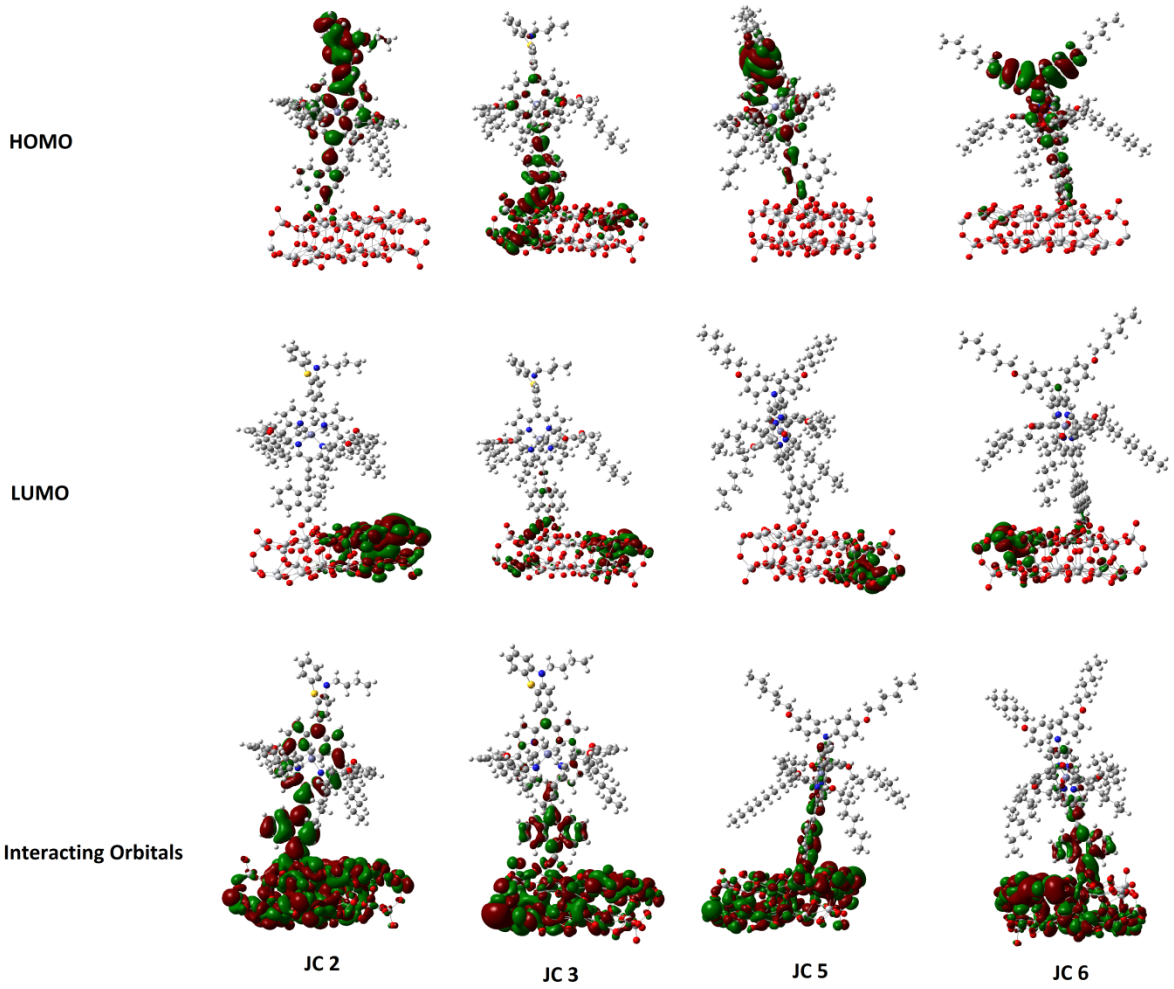

Figure S9. (a) HOMO (b) LUMO and (c) interacting orbital isosurfaces of JC2, JC3, JC5 and JC6 dyes on the $(TiO_2)_{36}$ nanoparticle. The isovalue is 0.001 a.u.