

Double-anchoring organic dyes for dye-sensitized solar cells: the opto-electronic property and performance

Table S1 Energy levels of dyes calculated by DFT/6-31G(d) in DMF

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Figure S1 Frontier molecular orbitals of dyes MA-201 – MA-206 and MA-2.

Figure S2 Optimized geometries of dyes on TiO₂ cluster (only one anchoring moiety adsorption to TiO₂)

Table S1 Energy levels of dyes calculated by DFT/6-31G(d) in DMF

	MA-2	MA-201	MA-202	MA-203	MA-204	MA-205	MA-206
L+2	-2.46	-1.70	-1.79	-2.12	-1.79	-1.96	-1.88
L+1	-2.54	-2.52	-2.53	-2.53	-2.50	-2.51	-2.51
L	-2.63	-2.60	-2.60	2.60	-2.59	-2.59	-2.58
H	-5.32	-5.07	-5.12	-5.08	-4.85	-4.96	-4.68
H-1	-5.53	-5.45	-5.50	-5.50	-5.39	-5.40	-5.37

Table S2 The FMO composition (%) of the individual groups for dye

Dye		H	L	L+1	L+2
MA-2	A ₁	3	2	70	0
	D ₁	53	4	27	0
	π -spacer	7	91	3	2
	D ₂	34	3	0	31
	A ₂	2	1	0	67
MA-201	A ₁	3	0	67	3
	D ₁	53	0	30	18
	π -spacer	23	1	2	51
	D ₂	19	34	1	26
	A ₂	1	64	1	2
MA-202	A ₁	2	1	69	2
	D ₁	40	0	29	19
	π -spacer	35	1	1	58
	D ₂	22	32	0	19
	A ₂	1	66	1	2
MA-203	A ₁	1	60	8	2
	D ₁	22	27	3	11
	π -spacer	38	3	2	72
	D ₂	37	3	27	11
	A ₂	2	6	60	3
MA-204	A ₁	2	4	63	3
	D ₁	32	2	29	18
	π -spacer	47	1	1	61
	D ₂	17	29	2	17
	A ₂	1	64	5	1
MA-205	A ₁	3	12	54	2
	D ₁	41	6	26	13
	π -spacer	38	1	1	76
	D ₂	17	24	5	9
	A ₂	1	57	13	1
MA-206	A ₁	1	66	1	1
	D ₁	12	31	0	12
	π -spacer	71	1	1	72
	D ₂	16	0	29	13
	A ₂	1	1	69	2

Table S3 Absorption properties of dyes in DMF solution calculated at the CAM-B3LYP/6-31G(d) level

Dye	State	E_g / λ_{\max}	f	main configurations
MA-2	1	2.74/452	0.7044	H→L/0.59913
	2	3.02/411	0.4395	H→L+1/0.42346
	3	3.09/402	0.1866	H→L+2/0.39541
	4	3.34/371	0.0767	H-1→L/0.59813
	5	3.71/334	0.0484	H-2→L/0.53810
	6	4.01/309	0.0296	H→L+4/0.30999
MA-201	1	2.82/439	1.1196	H→L+1/0.51485
	2	3.05/407	0.8622	H-1→L/0.51160
	3	3.56/348	0.9752	H→L+2/0.55304
	4	3.98/311	0.1977	H→L+3/0.39019
	5	4.04/307	0.1527	H-4→L+1/0.30361
	6	4.07/305	0.0696	H-5→L/0.31842
MA-202	1	3.00/414	1.7312	H→L/0.38446
	2	3.10/400	0.6524	H→L+1/0.37626
	3	3.47/357	0.7173	H→L+2/0.56013
	4	4.05/306	0.0170	H-5→L/0.31234
	5	4.10/303	0.0515	H-1→L+2/0.27903
	6	4.13/301	0.0544	H→L/0.31804
MA-203	1	2.82/439	1.5308	H→L+2/0.46824
	2	3.08/403	0.7822	H-1→L/0.39951
	3	3.20/387	0.3009	H→L+2/0.38065
	4	3.99/311	0.0001	H-1→L+2/0.50291
	5	4.07/304	0.0334	H-4→L/0.37084
	6	4.10/303	0.0845	H-3→L+1/0.34296
MA-204	1	2.77/447	1.4343	H→L+1/0.38859
	2	2.98/415	1.0761	H-1→L/0.38501
	3	3.24/382	0.4924	H→L+2/0.50770
	4	3.86/321	0.0987	H→L/0.49334
	5	3.94/315	0.0045	H→L+1/0.40435
	6	3.97/313	0.0433	H→L+3/0.36275
MA-205	1	2.78/446	1.2388	H→L+2/0.36905

	2	2.99/415	1.1965	H-1→L/0.38131
	3	3.17/391	0.2227	H→L+2/0.45767
	4	3.94/314	0.0221	H-1→L+2/0.42259
	5	3.98/312	0.0760	H→L/0.40889
	6	4.04/307	0.0336	H-3→L+1/0.30766
MA-206	1	2.71/458	2.4062	H→L+2/0.55787
	2	3.01/412	0.6791	H-1→L/0.34804
	3	3.13/396	0.3202	H-1→L+1/0.35193
	4	3.69/336	0.1339	H→L/0.52766
	5	3.74/331	0.0812	H→L+1/0.50059
	6	3.80/326	0.0026	H→L+3/0.47480

Table S4 Energy levels of dyes calculated by DFT/6-31G(d) in DMF after binding on the TiO₂

	H	L	ΔE_{H-L}
MA-2T1	-5.35	-3.27	2.08
MA-201T1	-5.06	-3.28	1.78
MA-202T1	-5.10	-3.26	1.84
MA-203T1	-5.09	-3.28	1.81
MA-204T1	-4.85	-3.29	1.56
MA-205T1	-4.95	-3.30	1.66
MA-206T1	-4.67	-3.28	1.39
MA-2T2	-5.36	-3.28	2.08
MA-201T2	-5.12	-3.30	1.82
MA-202T2	-5.13	-3.30	1.83
MA-203T2	-5.11	-3.28	1.83
MA-204T2	-4.90	-3.28	1.62
MA-205T2	-4.99	-3.27	1.72
MA-206T2	-4.67	-3.29	1.38

Dye/T1 represents only one anchoring moiety adsorption to TiO₂

Dye/T2 represents two anchoring moieties adsorption to TiO₂

Table S5 Absorption properties of dyes in DMF solution calculated at the CAM-B3LYP/6-31G(d) level after binding on the TiO₂

Dye	State	E_g / λ_{\max}	f	main configurations
MA-2T1	1	2.86/433	1.3623	H→L+3/0.43963
	2	3.06/406	0.7783	H→L+7/0.49831
	3	3.25/381	0.2438	H→L+9/0.49710
	4	3.82/324	0.0094	H-1→L+9/0.47011
	5	3.90/318	0.0135	H→L/0.58291
	6	3.93/316	0.3832	H-9→L+3/0.20062
MA-201T1	1	2.79/444	1.2545	H→L+8/0.48065
	2	2.89/429	0.9677	H-1→L+3/0.42936
	3	3.54/350	0.9789	H-1→L+8/0.18849
	4	3.71/334	0.0046	H→L/0.65720
	5	3.84/323	0.0673	H→L+3/0.54129
	6	3.92/316	0.0000	H→L+1/0.66573
MA-202T1	1	2.82/439	1.6661	H-1→L+3/0.39575
	2	3.05/406	1.0447	H→L+8/0.40067
	3	3.42/363	0.6705	H-1→L+8/0.21116
	4	3.75/331	0.0002	H→L/0.65731
	5	3.90/318	0.0152	H→L+3/0.45183
	6	3.92/316	0.0003	H→L+1/0.63521
MA-203T1	1	2.75/450	1.6316	H→L+3/0.37292
	2	2.98/417	0.8932	H→L+8/0.29596
	3	3.18/389	0.3845	H→L+14/0.27462
	4	3.72/334	0.0012	H→L/0.66174
	5	3.88/319	0.0591	H→L+3/0.49248
	6	3.91/317	0.0000	H→L+1/0.66345
MA-204T1	1	2.73/455	1.4503	H-1→L+3/0.31198
	2	2.87/431	1.1998	H→L+8/0.37020
	3	3.21/386	0.6087	H→L+18/0.52591
	4	3.49/356	0.0071	H→L/0.68593
	5	364/341	0.1591	H→L+3/0.53165

	6	3.70/336	0.0003	H→L+1/0.68744
MA-205T1	1	2.71/458	1.2225	H→L+3/0.30600
	2	2.87/432	1.4103	H→L+8/0.37832
	3	3.12/398	0.3298	H→L+15/0.38410
	4	3.57/347	0.0037	H→L/0.67758
	5	3.73/333	0.0928	H→L+3/0.53743
	6	3.77/329	0.0009	H→L+1/0.67253
MA-206T1	1	2.69/460	2.1901	H→L+17/0.46811
	2	2.90/427	1.1481	H→L+17/0.30197
	3	3.11/399	0.2736	H-1→L+8/0.41088
	4	3.33/373	0.0181	H→L/0.68742
	5	3.45/359	0.1657	H→L+3/0.55030
	6	3.53/351	0.0001	H→L+1/0.69802
MA-2T2	1	2.82/439	1.3786	H→L+6/0.44423
	2	2.92/425	1.0984	H-1→L+6/0.43939
	3	3.20/387	0.2118	H→L+16/0.41238
	4	3.81/325	0.0105	H-1→L+16/0.42968
	5	3.87/320	0.0031	H→L/0.60712
	6	3.90/318	0.0828	H→L+1/0.50994
MA-201T2	1	2.63/472	1.4300	H→L+6/0.45838
	2	2.86/433	1.1245	H→L+7/0.32315
	3	3.51/353	0.9286	H-2→L+6/0.20926
	4	3.61/344	0.0214	H→L+1/0.64994
	5	3.72/333	0.0010	H→L/0.65006
	6	3.82/325	0.0000	H→L+3/0.64997
MA-202T2	1	2.79/444	2.1888	H→L+6/0.40192
	2	2.87/432	0.7014	H-1→L+6/0.42178
	3	3.38/367	0.8093	H→L+32/0.56328
	4	3.72/333	0.0008	H→L/0.65964
	5	3.74/332	0.0004	H→L+1/0.65809
	6	3.86/321	0.0408	H→L+7/0.42417
MA-203T2	1	2.73/455	1.8314	H→L+6/0.37495
	2	2.89/429	0.9189	H→L+7/0.37559
	3	3.08/403	0.4754	H→L+24/0.42822
	4	3.72/334	0.0021	H→L/0.66404

	5	3.74/332	0.0019	H→L+1/0.66644
	6	3.86/321	0.0659	H→L+6/0.37937
MA-204T2	1	2.63/471	1.4318	H→L+6/0.44636
	2	2.81/442	1.3371	H→L+7/0.38581
	3	3.19/389	0.7705	H→L+34/0.27388
	4	3.50/354	0.0012	H→L+1/0.67909
	5	3.53/351	0.0059	H→L/0.68439
	6	3.65/340	0.1245	H→L+7/0.53089
MA-205T2	1	2.62/474	1.2914	H→L+6/0.44708
	2	2.80/443	1.5458	H→L+7/0.38335
	3	3.08/402	0.4115	H→L+30/0.34438
	4	3.57/347	0.0005	H→L/0.66035
	5	3.63/342	0.0032	H→L+1/0.66932
	6	3.75/330	0.0786	H→L+7/0.50969
MA-206T2	1	2.63/472	2.5185	H→L+6/0.31561
	2	2.80/443	0.9309	H→L+7/0.36246
	3	2.98/416	0.4657	H-1→L+7/0.27886
	4	3.31/374	0.0107	H→L/0.69218
	5	3.33/373	0.0132	H→L+1/0.68932
	6	3.45/360	0.1679	H→L+6/0.44191

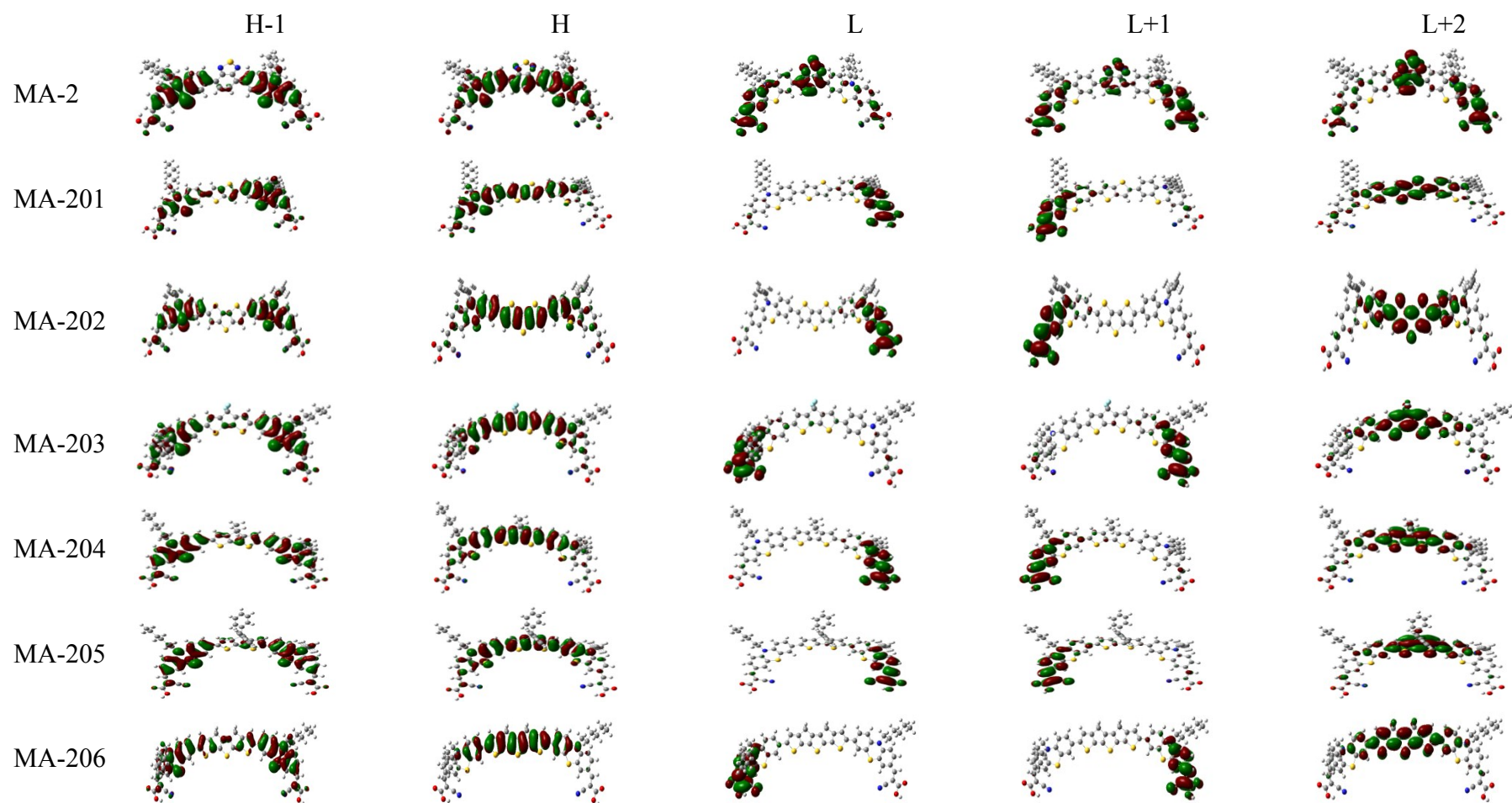
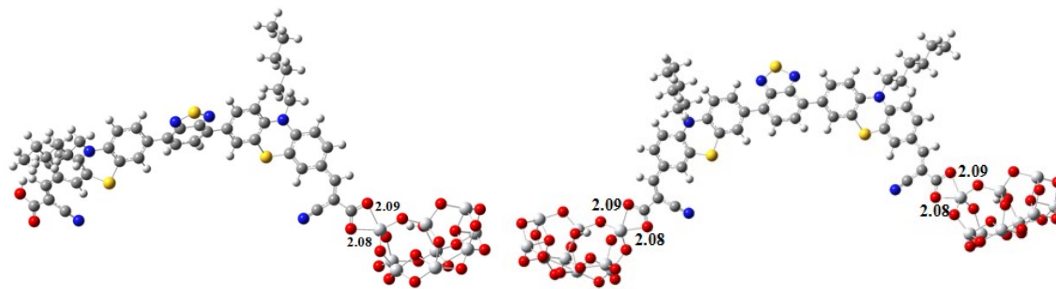
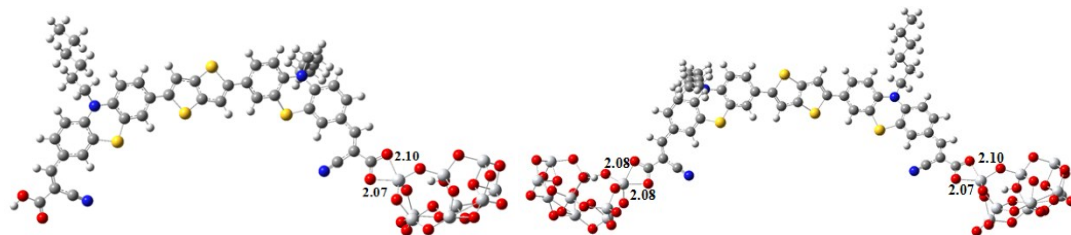


Figure S1 Frontier molecular orbitals of dyes MA-201 – MA-206 and MA-2.



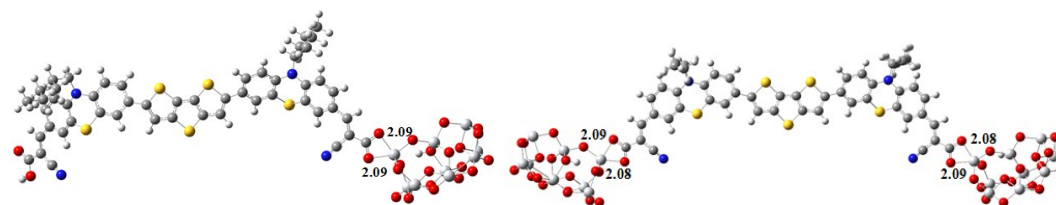
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MA-2T2



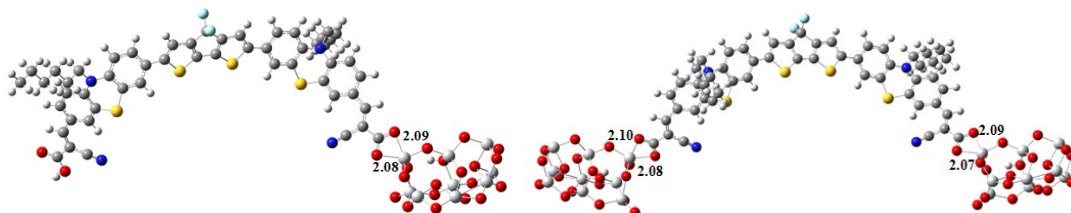
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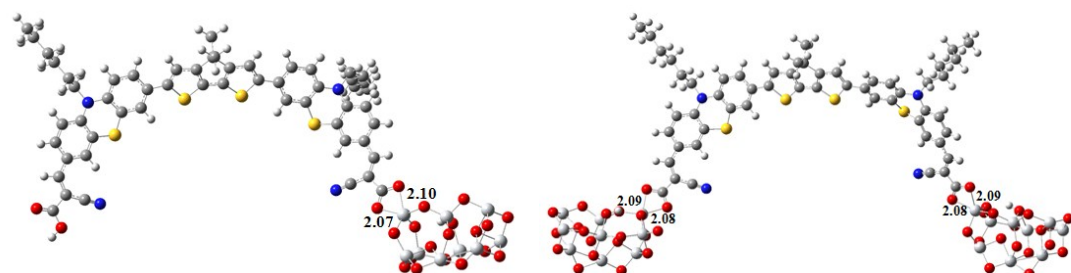
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MA-202T2



MA-203T1

MA-203T2



MA-204T1

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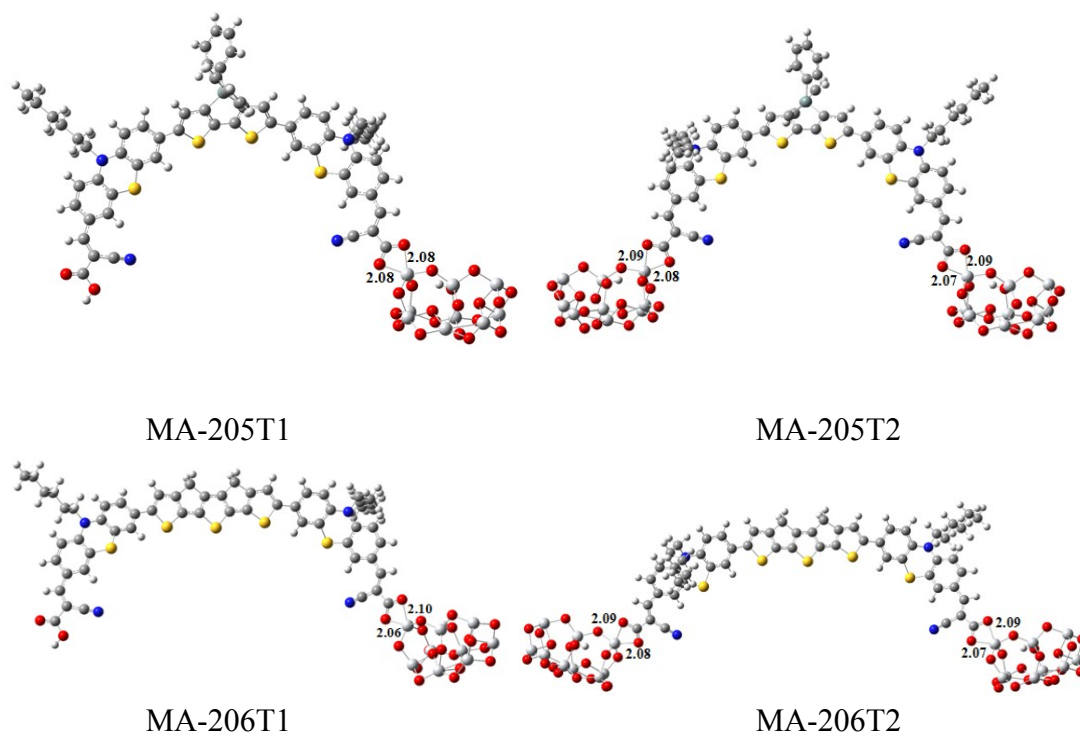


Figure S2 Optimized geometries of dyes on TiO_2 cluster (only one anchoring moiety adsorption to TiO_2)