Interplay Between TiO_2 Surfaces and Organic Photochromes: A DFT Study Of Adsorbed Azobenzenes and Diarylethenes

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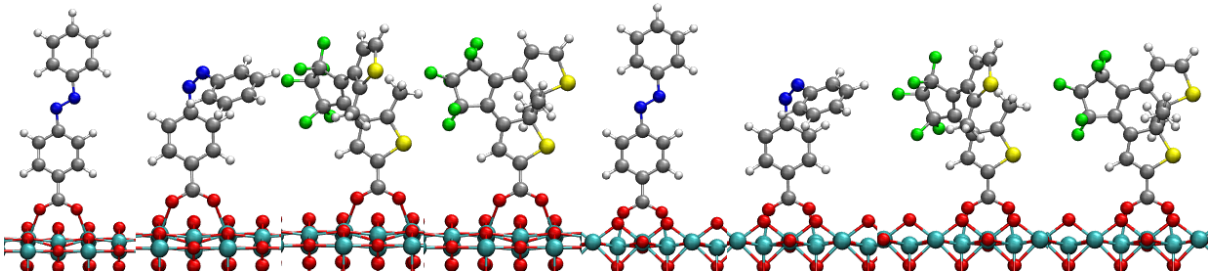
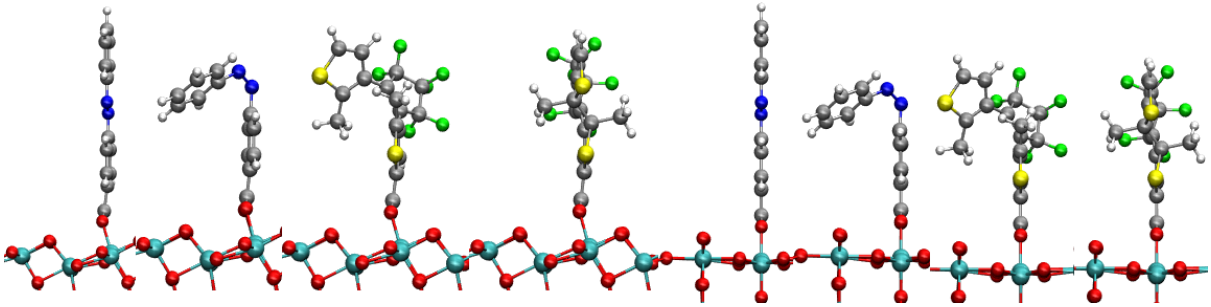
Rutile and anatase refer to the rutile (110) and anatase (101) cuts of TiO_2 throughout. See computational section of paper for further details.

Table S-I: Comparison of our calculated lattice parameters for rutile and anatase with those reported by Labat et al.[1]

Material	a	c
Anatase (This work)	3.798	9.738
Rutile (This work)	4.612	2.970
Anatase (Ref. 1)	3.786	9.867
Rutile (Ref. 1)	4.653	2.975



(a) Front views



(b) Side views

Figure S-1: Adsorbed structures of *trans*-/*cis*-AZB and open-/closed-DTE on anatase (101) (four leftmost) and rutile (110) (four rightmost).

Table S-II: Comparison between the binding energies (eV) computed with gamma grid and 2x2x1 grid

		1x1x1		2x2x1	
Photochrome	State	Anatase	Rutile	Anatase	Rutile
AZB	cis	-1.163	-2.717	-1.161	-2.703
AZB	trans	-1.085	-2.671	-1.079	-2.649
DTE	closed	-1.167	-2.714	-1.140	-2.718
DTE	open	-1.128	-2.717	-1.136	-2.709

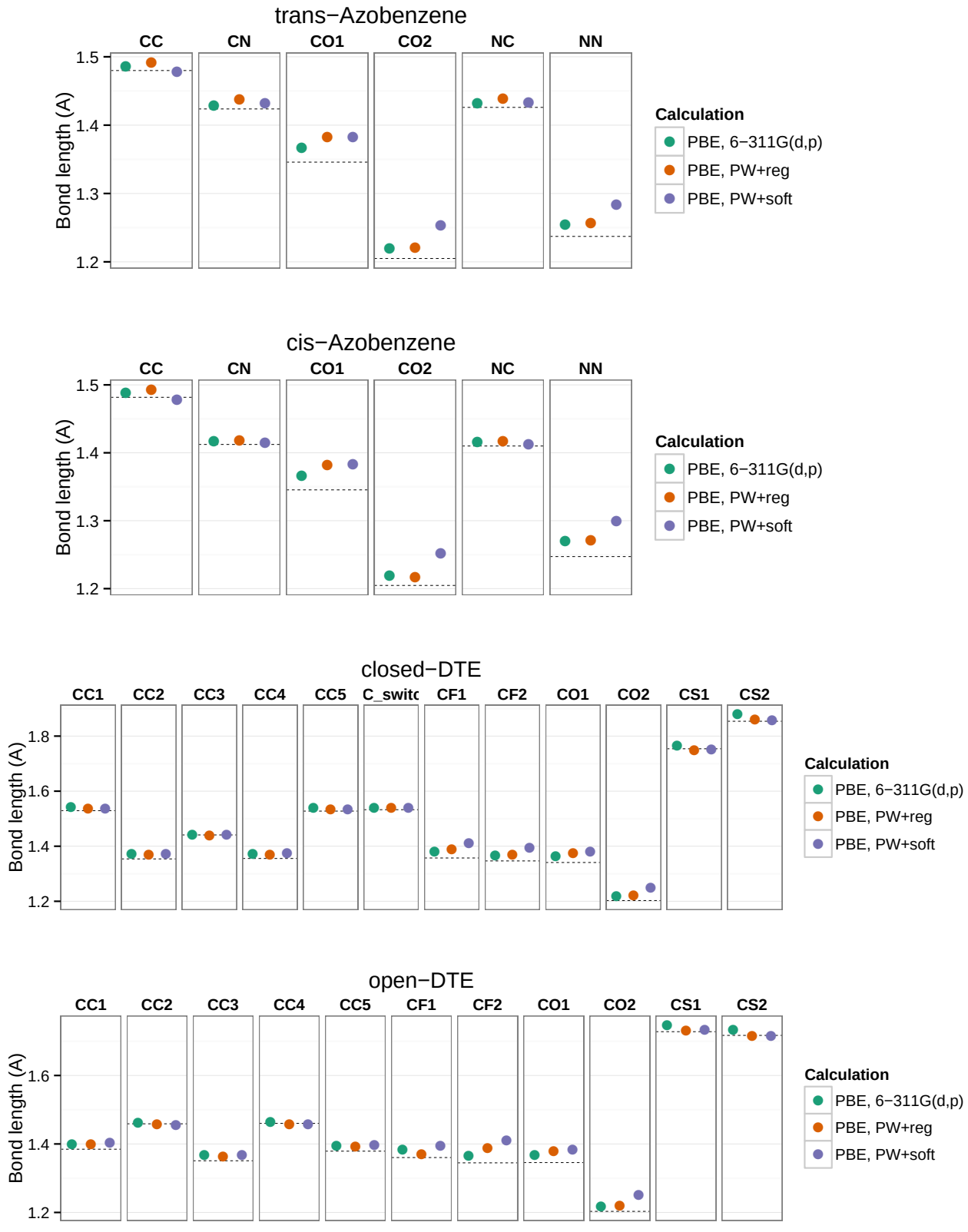
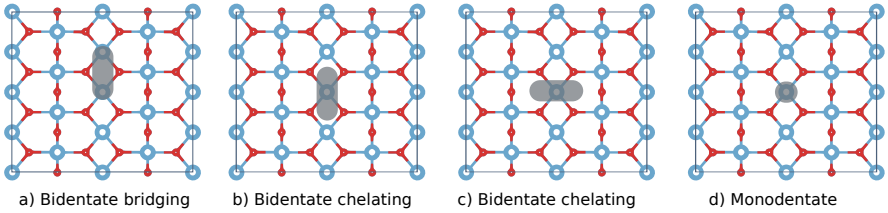
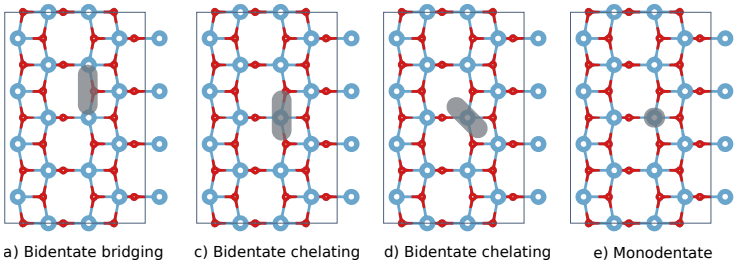


Figure S-2: Comparison of selected bond lengths (Å) calculated at PBE/6-311G(d,p) using Gaussian09, PBE with regular pseudopotentials at 400 eV cut-off with VASP, and PBE with soft pseudopotentials at 300 eV cut-off with VASP. Bond lengths calculated with PBE0/6-311G(d,p) in Gaussian09 are shown in dotted line for reference.



(a) Rutile (110)



(b) Anatase (101)

Figure S-3: Binding sites considered

Table S-III: Binding energies in eV

Photochrome	State	Anatase	Rutile
AZB	trans	-1.097	-2.679
AZB	cis	-1.166	-2.715
AZB-$(CN)_3$	trans	-1.080	-2.556
AZB-$(CN)_3$	cis	-1.100	-2.603
AZB-NMe_2	trans	-1.122	-2.769
AZB-NMe_2	cis	-1.127	-2.887
DTE	open	-1.136	-2.725
DTE	closed	-1.174	-2.724
DTE-$(CN)_3$	open	-1.139	-2.656
DTE-$(CN)_3$	closed	-1.125	-2.629
DTE-NMe_2	open	-1.198	-2.899
DTE-NMe_2	closed	-1.202	-2.931
DTE-ThPh	open	-1.149	-2.730
DTE-ThPh	closed	-1.203	-2.848
inverse-DTE	open	-1.122	-2.730
inverse-DTE	closed	-1.149	-2.723
inverse-DTE-ThPh	open	-1.134	-2.755
inverse-DTE-ThPh	closed	-1.178	-2.771
DTE (link=Ph)	open	-1.116	-2.707
DTE (link=Ph)	closed	-1.121	-2.753
DTE-Ph (link=Ph)	open	-1.128	-2.754
DTE-Ph (link=Ph)	closed	-1.124	-2.804
DTE (link=ThPh)	open	-1.160	-2.760
DTE (link=ThPh)	closed	-1.132	-2.743
DTE (ring=maleimide)	open	-1.154	-2.730
DTE (ring=maleimide)	closed	-1.142	-2.735
DTE (ring=pentene)	open	-1.192	-2.799
DTE (ring=pentene)	closed	-1.226	-3.033

Table S-IV: C-C bond lengths for the anchor-phytochrome bond in Å.

Photochrome	State	Gas	Anatase	Rutile
AZB	trans	1.478	1.476	1.455
AZB	cis	1.478	1.472	1.452
AZB-$(CN)_3$	trans	1.484	1.480	1.463
AZB-$(CN)_3$	cis	1.484	1.481	1.464
AZB-NMe_2	trans	1.472	1.471	1.454
AZB-NMe_2	cis	1.470	1.469	1.452
DTE	open	1.460	1.458	1.434
DTE	closed	1.468	1.468	1.453
DTE-$(CN)_3$	open	1.462	1.460	1.439
DTE-$(CN)_3$	closed	1.473	1.473	1.457
DTE-NMe_2	open	1.460	1.457	1.440
DTE-NMe_2	closed	1.465	1.466	1.450
DTE-ThPh	open	1.462	1.455	1.441
DTE-ThPh	closed	1.469	1.468	1.457
inverse-DTE	open	1.461	1.462	1.435
inverse-DTE	closed	1.470	1.472	1.458
inverse-DTE-ThPh	open	1.460	1.458	1.438
inverse-DTE-ThPh	closed	1.470	1.482	1.458
DTE (link=Ph)	open	1.478	1.474	1.451
DTE (link=Ph)	closed	1.479	1.482	1.464
DTE-Ph (link=Ph)	open	1.478	1.472	1.449
DTE-Ph (link=Ph)	closed	1.477	1.478	1.461
DTE (link=ThPh)	open	1.458	1.450	1.424
DTE (link=ThPh)	closed	1.462	1.465	1.449
DTE (ring=maleimide)	open	1.458	1.460	1.440
DTE (ring=maleimide)	closed	1.470	1.471	1.456
DTE (ring=pentene)	open	1.451	1.446	1.428
DTE (ring=pentene)	closed	1.455	1.463	1.451

Table S-V: Absolute bond length alternation (BLA, Å).

Photochrome	State	Gas	Anatase	Rutile
AZB	trans	0.117	0.117	0.117
AZB	cis	0.152	0.151	0.137
AZB-$(CN)_3$	trans	0.112	0.111	0.116
AZB-$(CN)_3$	cis	0.145	0.144	0.147
AZB-NMe_2	trans	0.097	0.096	0.091
AZB-NMe_2	cis	0.128	0.129	0.123
DTE	open	-0.086	-0.091	-0.090
DTE	closed	0.068	0.066	0.051
DTE-$(CN)_3$	open	-0.089	-0.089	-0.090
DTE-$(CN)_3$	closed	0.058	0.056	0.049
DTE-NMe_2	open	-0.086	-0.086	-0.088
DTE-NMe_2	closed	0.055	0.048	0.032
DTE-ThPh	open	-0.088	-0.090	-0.090
DTE-ThPh	closed	0.057	0.052	0.035
inverse-DTE	open	-0.069	-0.071	-0.070
inverse-DTE	closed	0.100	0.096	0.085
inverse-DTE-ThPh	open	-0.063	-0.063	-0.063
inverse-DTE-ThPh	closed	0.101	0.092	0.090
DTE (link=Ph)	open	-0.087	-0.083	-0.083
DTE (link=Ph)	closed	0.072	0.067	0.056
DTE-Ph (link=Ph)	open	-0.085	-0.085	-0.086
DTE-Ph (link=Ph)	closed	0.063	0.059	0.045
DTE (link=ThPh)	open	-0.087	-0.087	-0.088
DTE (link=ThPh)	closed	0.066	0.063	0.049
DTE (ring=maleimide)	open	-0.075	-0.074	-0.075
DTE (ring=maleimide)	closed	0.071	0.068	0.061
DTE (ring=pentene)	open	-0.101	-0.101	-0.094
DTE (ring=pentene)	closed	0.067	0.060	0.051

Table S-VI: Difference in the BLA (ΔBLA, Å) between photochromic states calculated as BLA(*cis*-AZB − *trans*-AZB) or BLA(open-DTE − closed-DTE).

Photochrome	Gas	Anatase	Rutile
AZB	0.035	0.034	0.021
AZB-$(CN)_3$	0.033	0.032	0.031
AZB-NMe_2	0.030	0.033	0.032
DTE	-0.018	-0.024	-0.039
DTE-$(CN)_3$	-0.032	-0.033	-0.041
DTE-NMe_2	-0.032	-0.038	-0.056
DTE-ThPh	-0.031	-0.039	-0.055
inverse-DTE	0.031	0.025	0.015
inverse-DTE-ThPh	0.037	0.029	0.027
DTE (link=Ph)	-0.014	-0.016	-0.027
DTE-Ph (link=Ph)	-0.021	-0.025	-0.041
DTE (link=ThPh)	-0.020	-0.024	-0.040
DTE (ring=maleimide)	-0.004	-0.006	-0.013
DTE (ring=pentene)	-0.034	-0.041	-0.042

PDOS

Three DOS figures are presented, in order: the unbound photochrome calculated with a 2x2x1 grid, the photochrome bound to anatase calculated with a 2x2x1 grid, and the photochrome bound to rutile calculated with a gamma grid. Projected p states of the photochrome in orange. Surface p, d states in light and dark gray respectively. Contributions of the anchor group in red. E_{HOMO} indicated with dotted line. Energies are aligned to the bare slab in which the scale is zeroed to E_{VBM}.

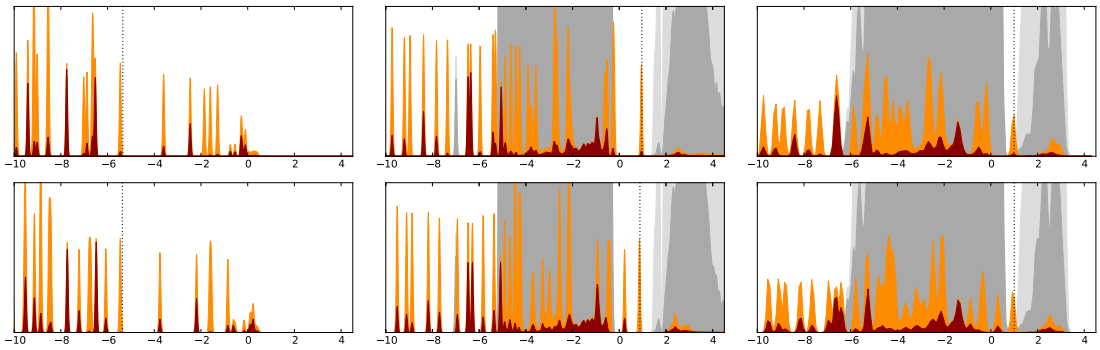


Figure S-4: AZB. Top: *cis* form, bottom: *trans* form

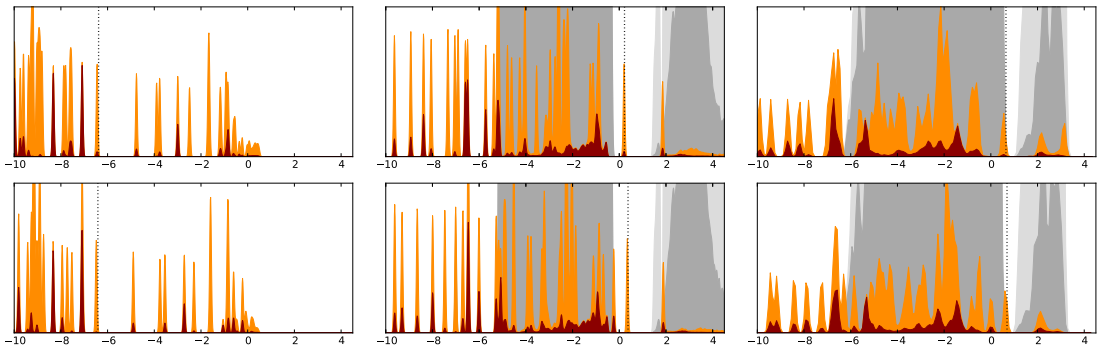


Figure S-5: AZB-$(CN)_3$. Top: *cis* form, bottom: *trans* form

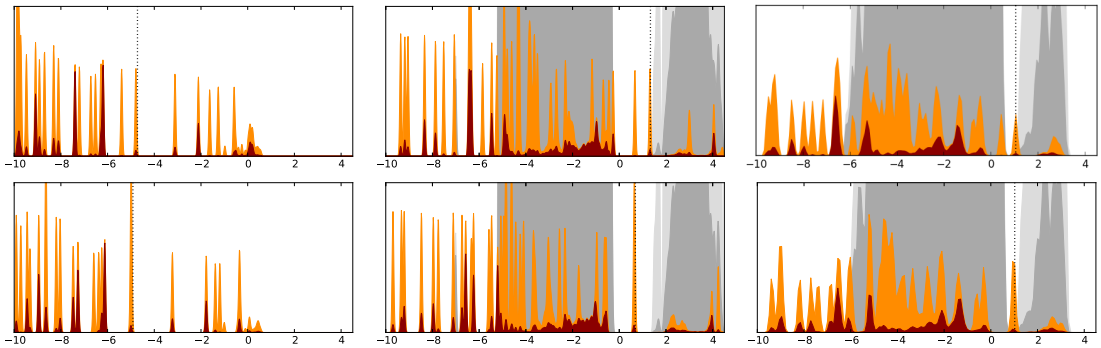


Figure S-6: AZB-NMe_2. Top: *cis* form, bottom: *trans* form

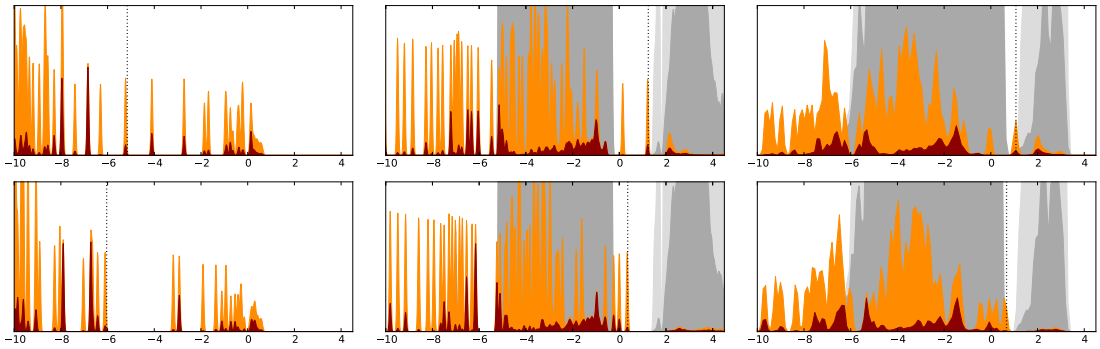


Figure S-7: DTE. Top: closed form, bottom: open form.

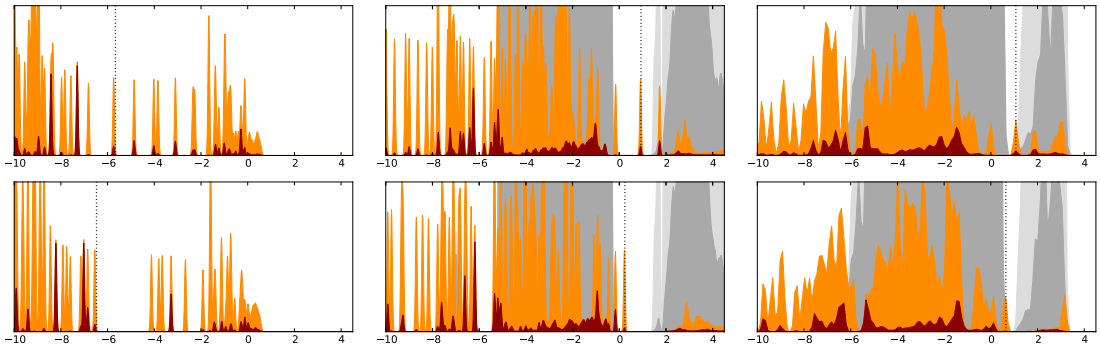


Figure S-8: DTE-$(CN)_3$. Top: closed form, bottom: open form.

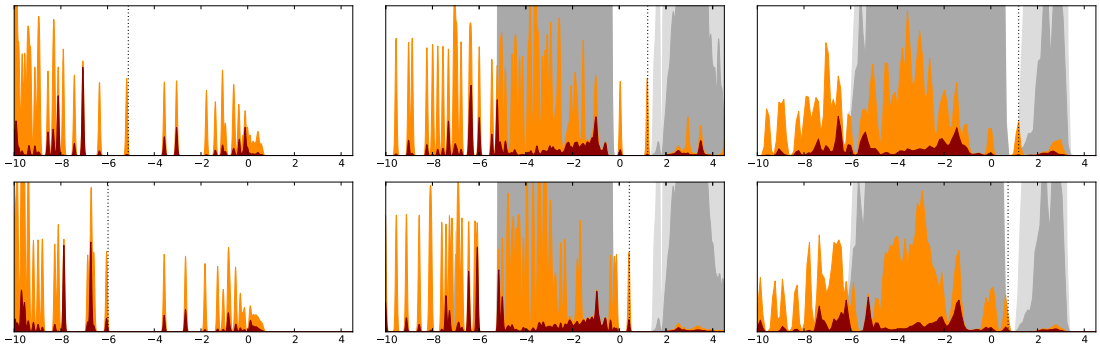


Figure S-9: inverse-DTE. Top: closed form, bottom: open form.

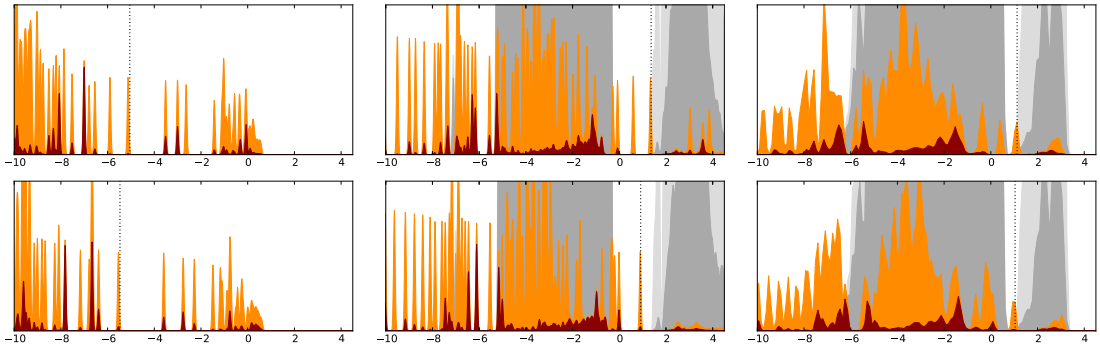


Figure S-10: inverse-DTE-ThPh. Top: closed form, bottom: open form.

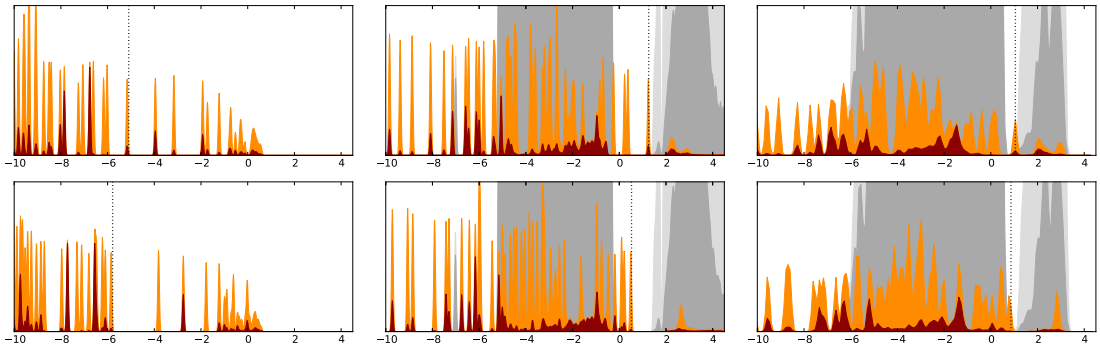


Figure S-11: DTE (ring=maleimide). Top: closed form, bottom: open form.

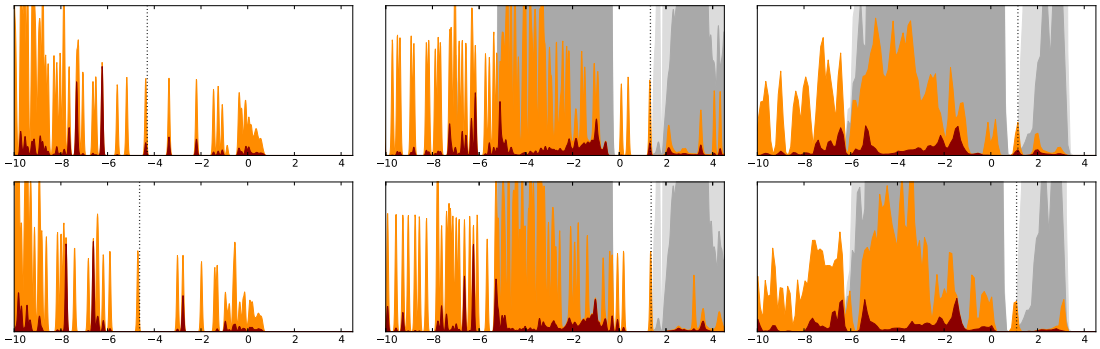


Figure S-12: DTE-NMe_2. Top: closed form, bottom: open form.

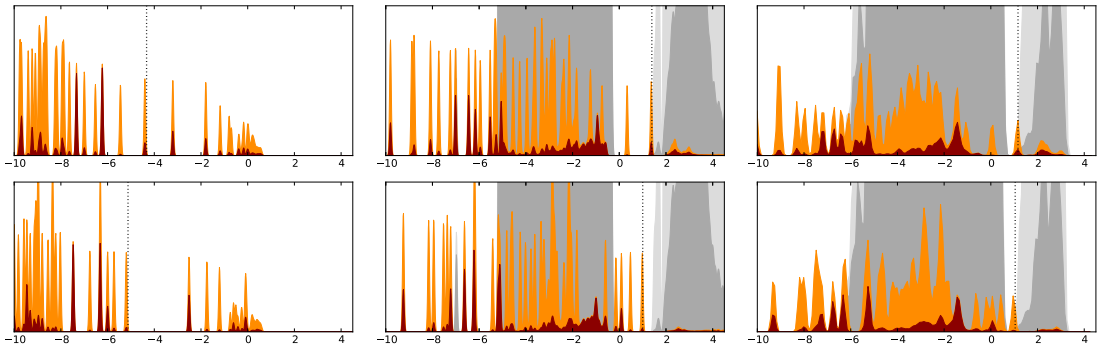


Figure S-13: DTE (ring=pentene). Top: closed form, bottom: open form.

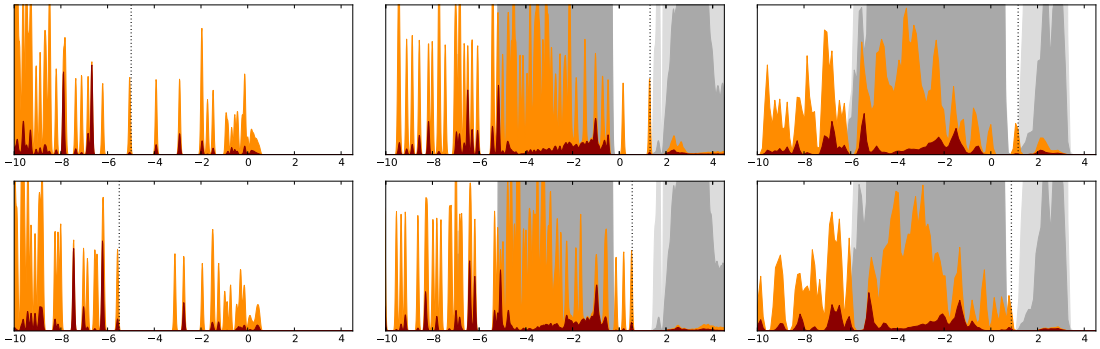


Figure S-14: DTE (link=Ph). Top: closed form, bottom: open form.

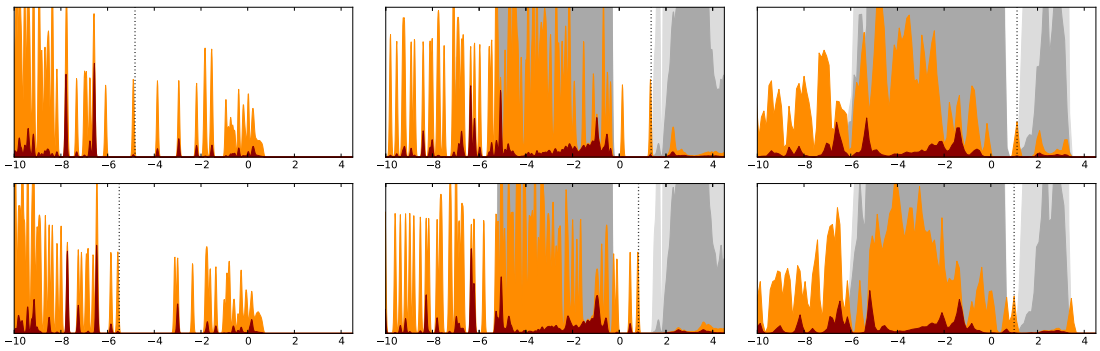


Figure S-15: DTE-Ph (link=Ph). Top: closed form, bottom: open form.

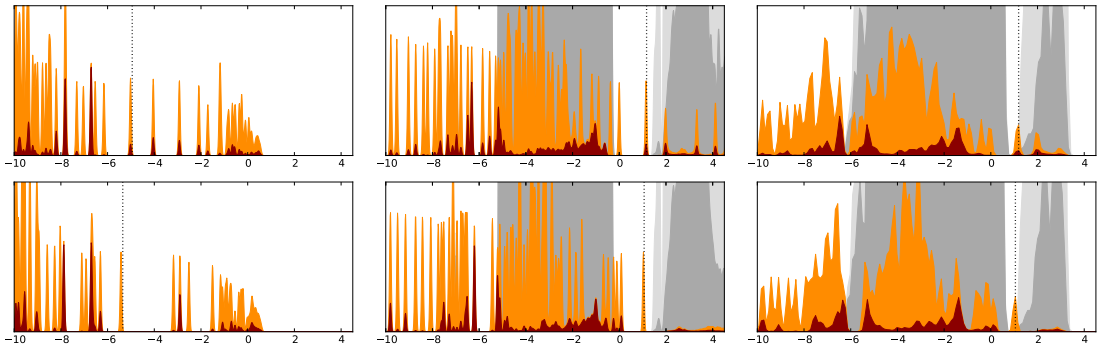


Figure S-16: DTE-ThPh. Top: closed form, bottom: open form.

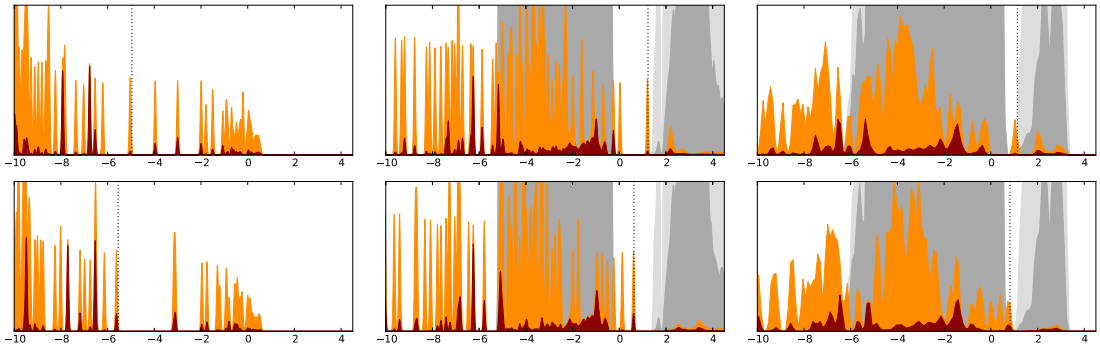


Figure S-17: DTE (link=ThPh). Top: closed form, bottom: open form.

Table S-VII: Energies of the valence ($E_{\mathbf{VBM}}$) and conduction bands ($E_{\mathbf{CBM}}$) of the anatase slab, HOMO ($E_{\mathbf{HOMO}}$) and LUMO ($E_{\mathbf{LUMO}}$) energies of the adsorbed photochrome on the anatase surface. All values in eV.

Photochrome	State	E_{VBM}	E_{CBM}	E_{HOMO}	E_{LUMO}	$\mathrm{E_{gap}}$
AZB	trans	-0.19	1.67	0.96	2.49	1.53
AZB	cis	-0.16	1.70	1.07	2.65	1.58
AZB-$(CN)_3$	trans	-0.17	1.69	0.46	2.00	1.54
AZB-$(CN)_3$	cis	-0.13	1.73	0.38	2.03	1.65
AZB-NMe_2	trans	-0.08	1.78	0.85	2.53	1.68
AZB-NMe_2	cis	-0.16	1.70	1.46	2.75	1.29
DTE	open	-0.19	1.67	0.44	2.66	2.22
DTE	closed	-0.16	1.70	1.34	2.29	0.94
DTE-$(CN)_3$	open	-0.12	1.74	0.39	2.77	2.38
DTE-$(CN)_3$	closed	-0.01	1.85	1.19	2.00	0.81
DTE-NMe_2	open	-0.18	1.68	1.45	2.64	1.19
DTE-NMe_2	closed	-0.16	1.70	1.43	2.24	0.81
DTE-ThPh	open	-0.16	1.70	1.14	2.67	1.53
DTE-ThPh	closed	-0.15	1.71	1.29	2.11	0.82
inverse-DTE	open	-0.17	1.69	0.53	2.65	2.12
inverse-DTE	closed	-0.01	1.85	1.49	2.83	1.33
inverse-DTE-ThPh	open	-0.19	1.67	0.99	2.61	1.62
inverse-DTE-ThPh	closed	0.37	2.23	2.00	3.11	1.11
DTE (link=Ph)	open	-0.18	1.68	0.62	2.61	2.00
DTE (link=Ph)	closed	-0.17	1.71	1.42	2.46	1.03
DTE-Ph (link=Ph)	open	-0.19	1.67	0.89	2.63	1.74
DTE-Ph (link=Ph)	closed	-0.17	1.69	1.45	2.42	0.97
DTE (link=ThPh)	open	-0.21	1.66	0.69	2.62	1.94
DTE (link=ThPh)	closed	-0.05	1.81	1.43	2.44	1.00
DTE (ring=maleimide)	open	-0.14	1.72	0.64	2.78	2.15
DTE (ring=maleimide)	closed	-0.14	1.72	1.39	2.38	0.99
DTE (ring=pentene)	open	-0.18	1.68	1.10	2.64	1.54
DTE (ring=pentene)	closed	-0.32	1.54	1.35	2.37	1.02

Table S-VIII: Dipole moments (Debye)

Photochrome	State	Anatase	Gas	Rutile
AZB	trans	-1.813	-2.810	-10.866
AZB	cis	1.588	0.321	-7.519
AZB-$(CN)_3$	trans	10.705	8.419	2.793
AZB-$(CN)_3$	cis	3.924	1.327	-3.873
AZB-NMe_2	trans	-8.903	-9.069	-18.649
AZB-NMe_2	cis	-3.297	-1.703	-19.335
DTE	open	0.638	-1.100	-7.250
DTE	closed	-0.020	-0.987	-10.879
DTE-$(CN)_3$	open	9.930	7.961	2.314
DTE-$(CN)_3$	closed	8.983	7.482	-2.049
DTE-NMe_2	open	-7.085	-5.019	-19.532
DTE-NMe_2	closed	-9.927	-9.229	-21.937
DTE-ThPh	open	-0.060	-1.538	-10.808
DTE-ThPh	closed	-3.403	-3.183	-14.672
inverse-DTE	open	2.244	0.164	-6.295
inverse-DTE	closed	2.931	2.882	-8.020
inverse-DTE-ThPh	open	0.355	-1.178	-9.777
inverse-DTE-ThPh	closed	1.668	2.002	-9.802
DTE (link=Ph)	open	-0.201	-0.992	-8.791
DTE (link=Ph)	closed	-1.008	0.507	-12.618
DTE-Ph (link=Ph)	open	-0.718	-1.789	-10.613
DTE-Ph (link=Ph)	closed	-3.121	-1.611	-16.234
DTE (link=ThPh)	open	-2.915	-3.543	-11.040
DTE (link=ThPh)	closed	-2.382	-2.159	-14.828
DTE (ring=maleimide)	open	-0.816	-2.144	-8.754
DTE (ring=maleimide)	closed	-0.666	-1.389	-11.163
DTE (ring=pentene)	open	-2.783	-3.097	-12.369
DTE (ring=pentene)	closed	-7.518	-4.441	-17.755

PCA Values

Table S-IX: Loadings for PCA carried out on the properties of the isolated photochromes

	Dim.1	Dim.2	Dim.3
BLA, gas	-0.71	0.11	0.70
dipole moment, gas	0.04	0.99	-0.12
E(gap), gas	0.71	0.06	0.70

Table S-X: Loadings for PCA carried out on the properties of the adsorbed systems

	Dim.1	Dim.2	Dim.3	Dim.4	Dim.5
Ti-O length	0.73	0.97	1.56	-0.40	-0.94
C-C length	0.75	1.31	-1.16	1.30	0.66
CBM movement	0.87	0.88	0.40	-2.67	1.14
E(binding)	1.38	-0.12	-0.85	0.73	1.58
BLA, ads	0.31	1.78	-1.15	0.61	0.15
Charge transfer	-1.03	0.56	1.68	1.15	1.25
Dipole moment, ads	1.39	-0.04	1.16	0.86	-0.24
E(gap), ads	0.59	-2.03	-0.00	0.15	0.42
E(HOMO), ads	-0.93	1.59	0.33	-0.65	1.08
E(LUMO), ads	-0.35	-1.38	0.52	-0.76	2.53
Δ E(HOMO)	1.43	0.06	1.21	0.08	-0.40
Δ E(LUMO)	1.30	0.87	0.40	0.24	-0.58

Table S-XI: PCA carried out on the properties of the isolated photochromes, cluster 1

	v.test	Mean in category	p.value
E(HOMO), ads	3.02	1.31	0.00
BLA, gas	2.72	0.08	0.01
BLA, ads	2.67	0.07	0.01
Δ E(HOMO)	-2.38	-0.10	0.02
Dipole moment, gas	-2.39	-3.37	0.02
E(gap), ads	-3.23	1.10	0.00
E(gap), gas	-3.44	1.26	0.00

Table S-XII: PCA carried out on the properties of the isolated photochromes, cluster 2

	v.test	Mean in category	p.value
Dipole moment, gas	2.90	3.94	0.00
BLA, ads	2.54	0.11	0.01
BLA, gas	2.51	0.11	0.01
Δ E(HOMO)	2.51	0.30	0.01
Δ E(LUMO)	2.46	0.16	0.01
CBM movement	2.21	-0.03	0.03
C-C length	2.19	1.48	0.03
Ti-O length	2.16	2.05	0.03

Table S-XIII: PCA carried out on the properties of the isolated photochromes, cluster 3

	v.test	Mean in category	p.value
E(gap), gas	4.21	2.39	0.00
E(gap), ads	3.58	1.88	0.00
E(LUMO), ads	2.95	2.67	0.00
E(HOMO), ads	-2.48	0.79	0.01
C-C length	-3.37	1.46	0.00
BLA, ads	-4.77	-0.09	0.00
BLA, gas	-4.79	-0.09	0.00

Table S-XIV: PCA carried out on the properties of the adsorbed systems, cluster 1

	v.test	Mean in category	p.value
charge.transfer	2.29	0.42	0.02
E(gap), ads	-1.97	1.08	0.05
Dipole moment, gas	-2.40	-5.15	0.02
Δ E(LUMO)	-2.67	-0.69	0.01
Dipole moment, ads	-2.68	-6.14	0.01
Δ E(HOMO)	-2.90	-0.26	0.00
E(binding)	-4.05	-1.20	0.00

Table S-XV: PCA carried out on the properties of the adsorbed systems, cluster 2

	v.test	Mean in category	p.value
E(gap), ads	3.93	2.01	0.00
E(gap), gas	3.82	2.43	0.00
E(LUMO), ads	2.58	2.68	0.01
C-C length	-2.10	1.46	0.04
E(HOMO), ads	-3.14	0.67	0.00
BLA, ads	-3.95	-0.08	0.00
BLA, gas	-3.96	-0.08	0.00

Table S-XVI: PCA carried out on the properties of the adsorbed systems, cluster 3

	v.test	Mean in category	p.value
BLA, ads	4.21	0.09	0.00
BLA, gas	4.18	0.10	0.00
C-C length	3.47	1.47	0.00
Δ E(LUMO)	2.61	-0.04	0.01
E(binding)	2.53	-1.13	0.01
CBM movement	2.40	-0.05	0.02
E(gap), ads	-2.08	1.26	0.04
E(gap), gas	-2.78	1.41	0.01

Table S-XVII: Difference of energies between the two photochromic states (eV)

Photochrome	Gas	Anatase	Rutile
AZB	0.464	0.395	0.428
AZB-$(CN)_3$	0.481	0.462	0.434
AZB-NMe_2	0.495	0.490	0.377

References

(1) Labat, F.; Baranek, P.; Adamo, C. Structural and Electronic Properties of Selected Rutile and Anatase TiO_2 Surfaces: An ab Initio Investigation. *J. Chem. Theory Comput.* **2008**, *4*, 341–352.