Electronic Supplementary Information for

Stack bonding in large polyaromatic hydrocarbons

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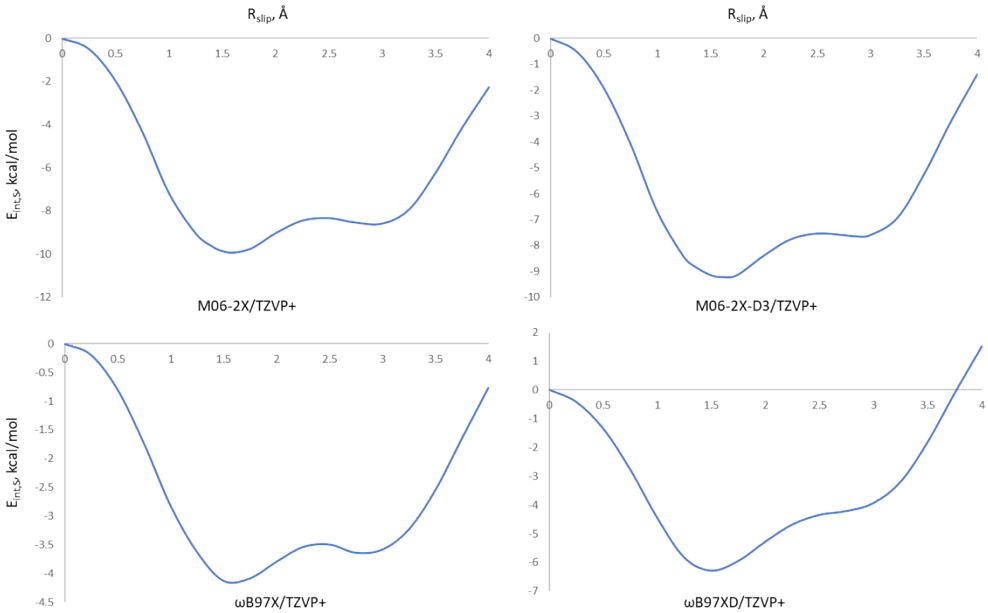

Figure S1. Potential energy curves along the PD-OV coordinate for **1**. Inclusion of the dispersion correction in the ωB97X-D functional masks the $PD_{II}OV_A$ minimum, which may reduce its predictive potential considering that this type of stacking is observable in the X-ray structure of γ-herringbone coronene.

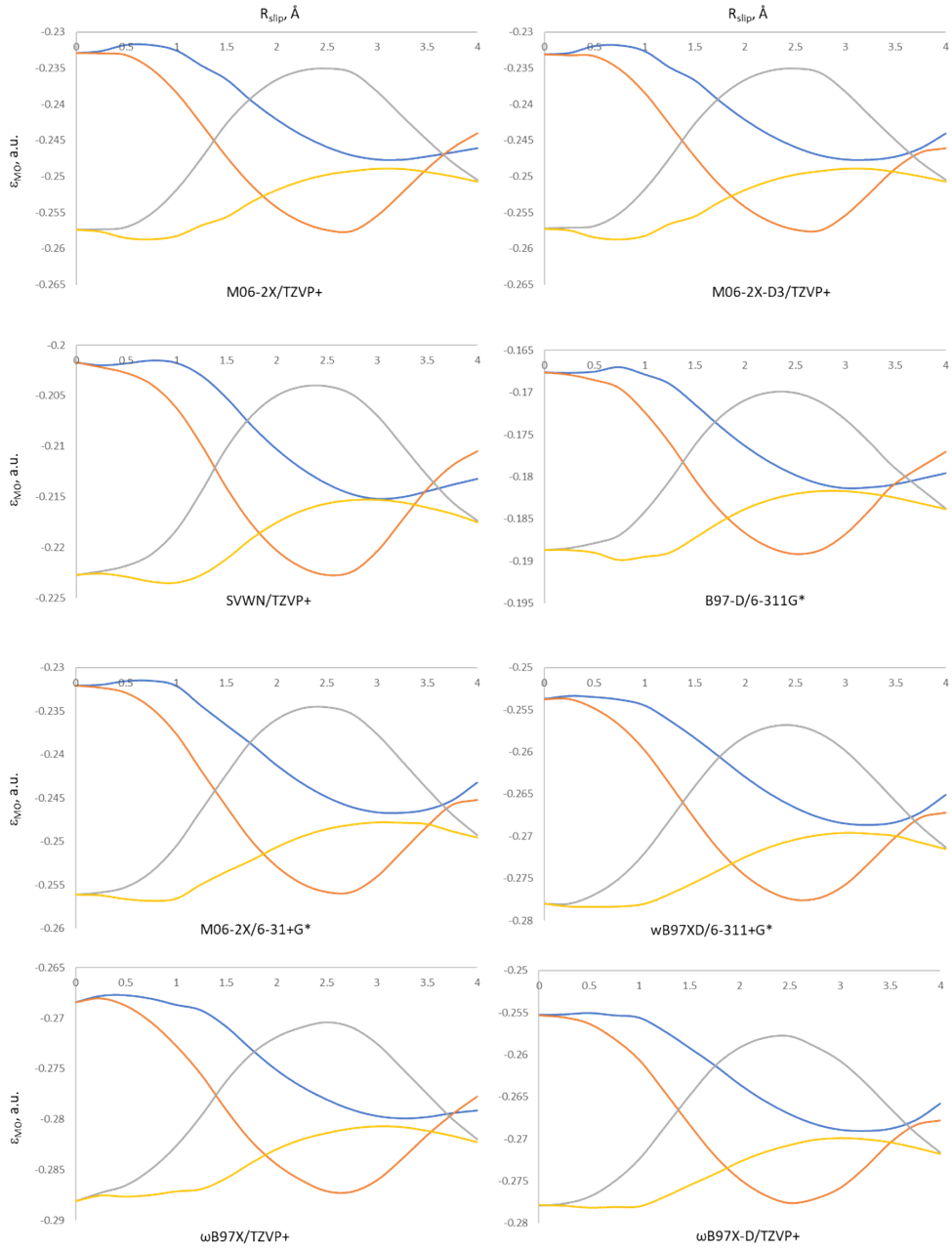

Figure S2. Walsh diagrams for dimers of **1** along the PD-OV coordinate with various combinations of functional and basis set. Note that the patterns are similar to those at the M06-2X/TZVP+ level.

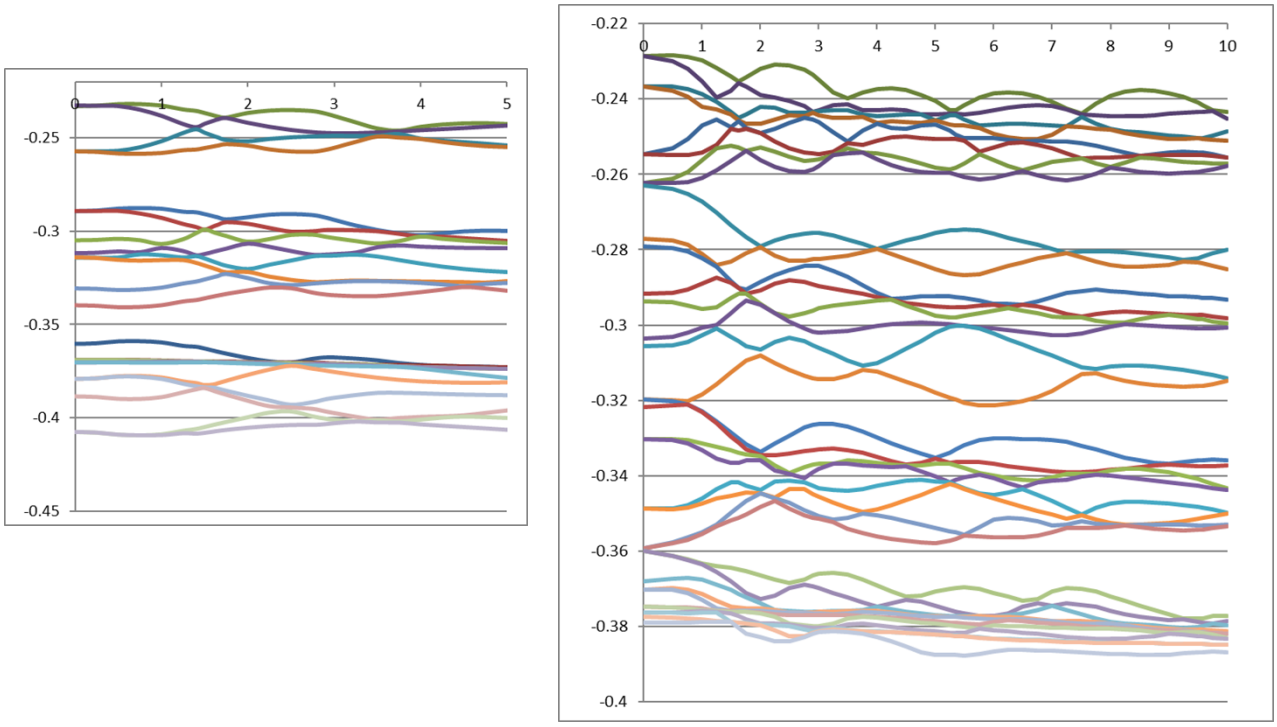

Figure S3. Extended Walsh diagrams for dimers of **1** and **4** along the PD-OV coordinate showing the bands of the MO energies. Only the highest energy frontier band is analyzed in depth, but mixing of monomer MOs in lower energy bands contribute to the overall SBO and follow similar patterns as the frontier band.

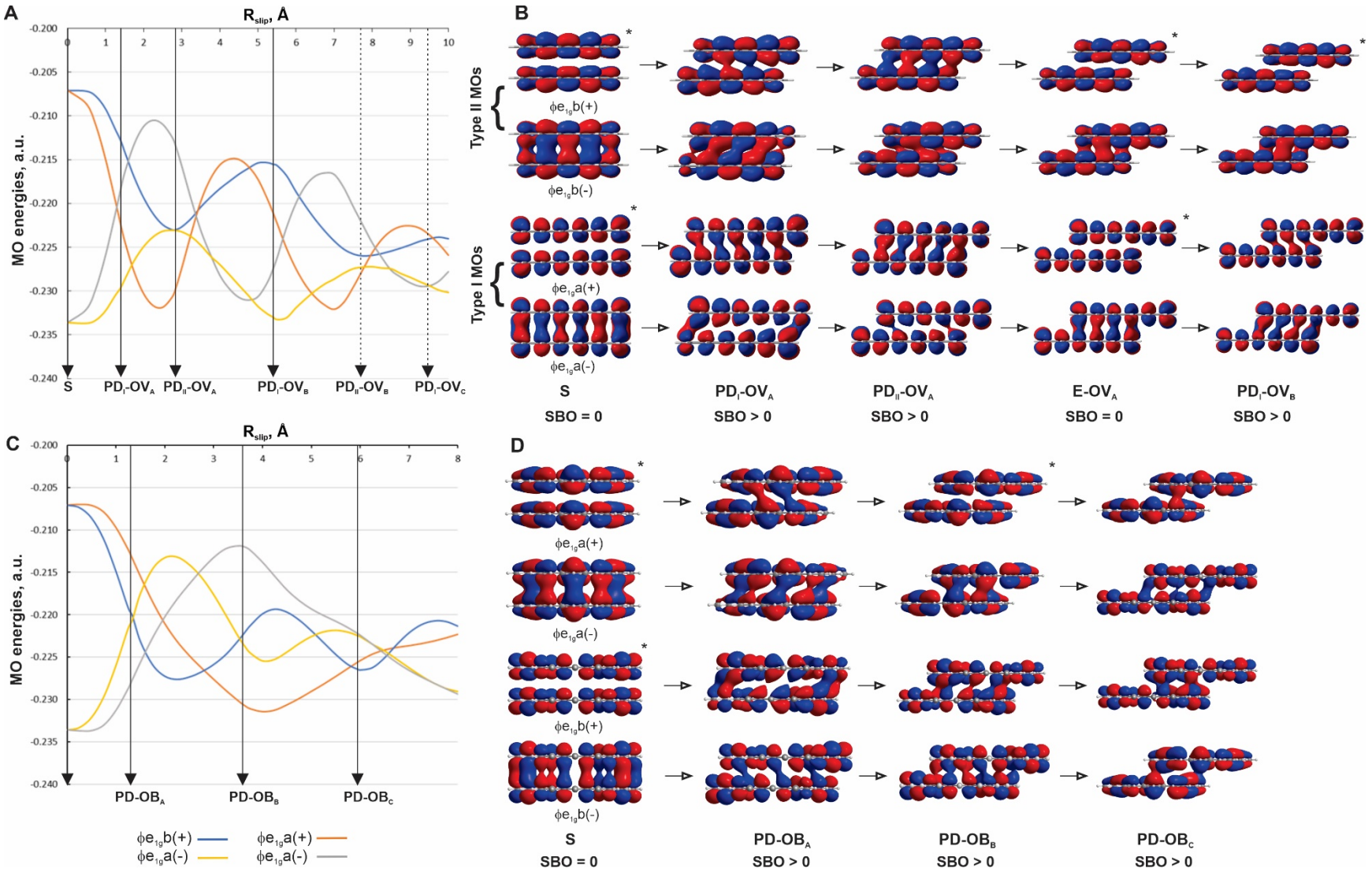

Figure S4. Walsh diagrams and changes in dimer MO character for **3** along the PD-OV and PD-OB coordinates.

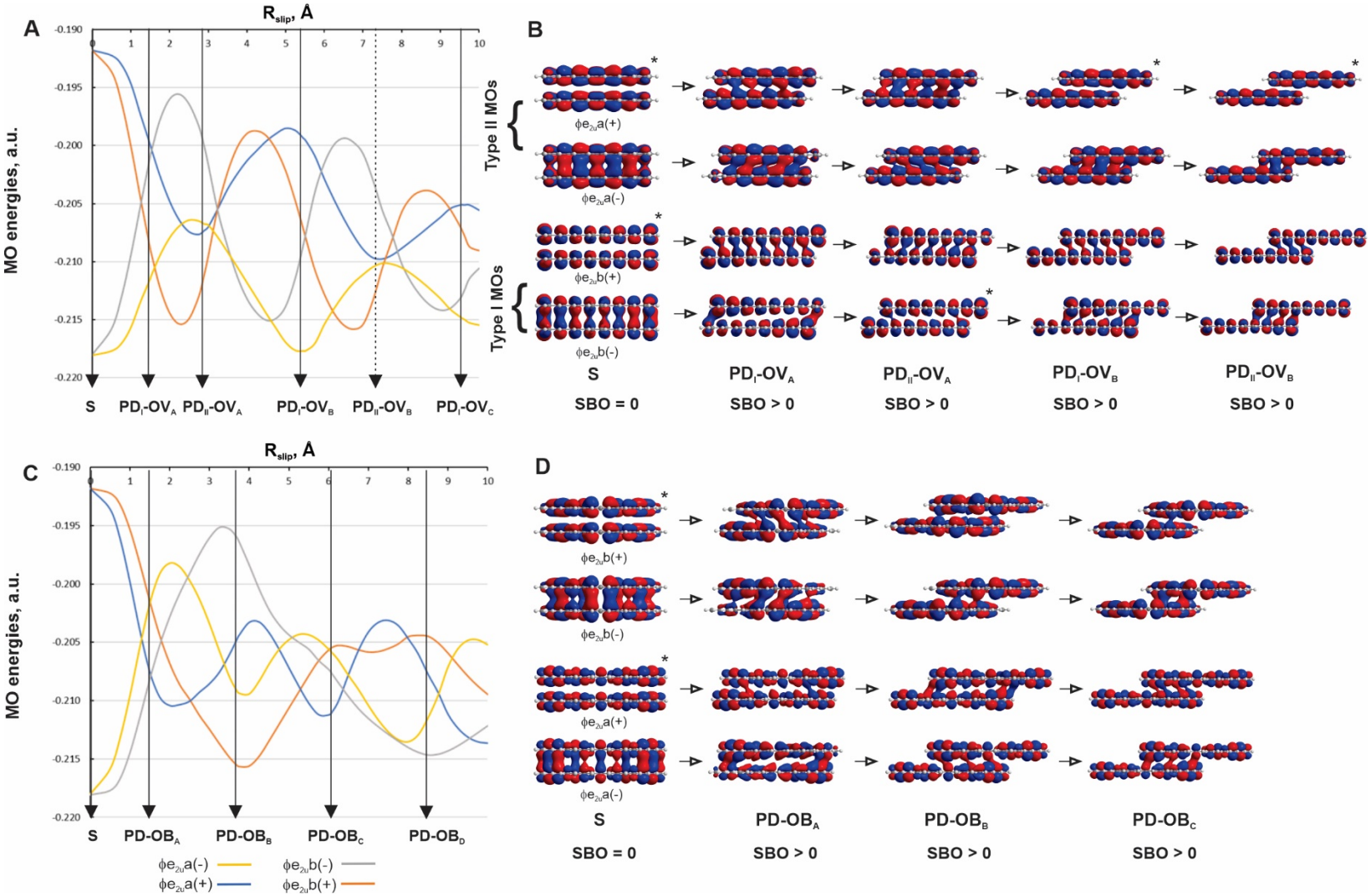

Figure S5. Walsh diagrams and changes in dimer MO character for **5** along the PD-OV and PD-OB coordinates.

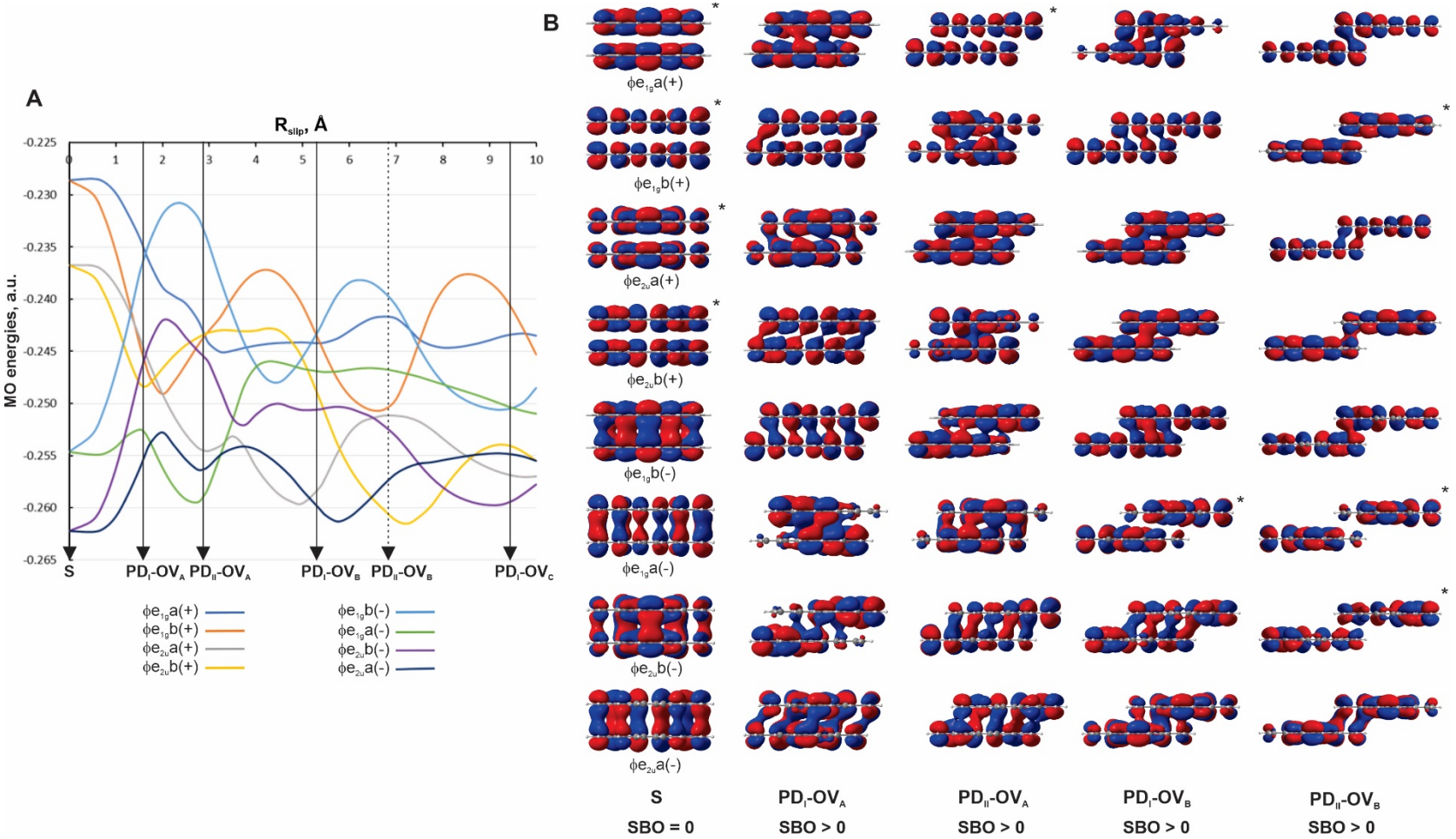

Figure S6A. Walsh diagrams (A) and changes in dimer MO character (B) for **4** along the PD-OV coordinates. Transitions between MOs are not indicated because MOs of the same irreducible representation mix heavily along the PD coordinates.

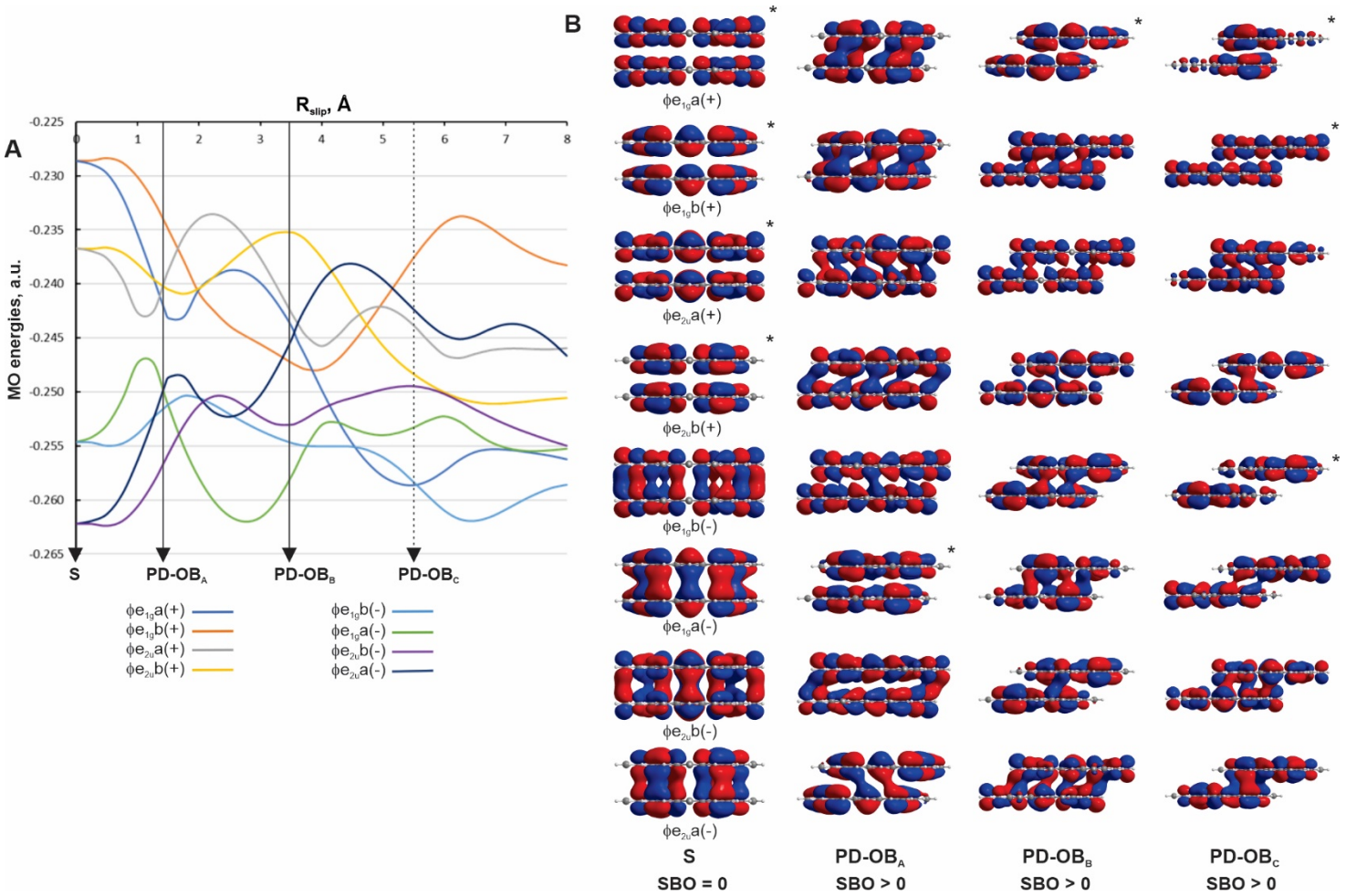

Figure S6B. Walsh diagrams (A) and changes in dimer MO character (B) for **4** along the PD-OB coordinates. Transitions between MOs are not indicated because MOs of the same irreducible representation mix heavily along the PD coordinates.

Table S1. Relative energies of parallel-displaced minima of PAH dimers

			M06-2X/6-31+g*		
			ΔE_{dimer}	R_{slip}, Å	R_{vert}, Å
1	S		-11.56 (0.00)	0.00	3.62
	PD_I	OV_A	-20.81 (-9.25)	1.61	3.35
	PD_{II}	OV_A	-19.25 (-7.69)	2.85	3.27
	PD	OB_A	-20.13 (-8.57)	1.41	3.36
	PD	OB_B	-14.95 (-3.38)	3.55	3.35
	TW		-19.94 (-8.38)	0.00	3.39
	TW-PD		-18.52 (-6.96)	2.00	3.37
2	S		-23.3 (0.00)	0.00	3.58
	PD_I	OV_A	-39.91 (-16.62)	1.60	3.34
	PD_{II}	OV_A	-37.70 (-14.41)	2.78	3.28
	PD_I	OV_B	-24.50 (-1.20)	5.60	3.29
	PD	OB_A	-38.92 (-15.62)	1.40	3.35
	PD	OB_B	-34.07 (-10.78)	3.69	3.31
	PD	OB_C	-23.14 (+0.15)	6.03	3.32
	TW		-35.80 (-12.51)	0.00	3.41
	TW-PD		-38.05 (-14.75)	1.06	3.37
3	S		-32.42 (0.00)	0.00	3.56
	PD_I	OV_A	-53.68 (-21.27)	1.56	3.33
	PD_{II}	OV_A	-51.32 (-18.91)	2.89	3.27
	PD_I	OV_B	-36.72 (-4.30)	5.37	3.24
	PD	OB_A	-52.03 (-19.61)	1.35	3.35
	PD	OB_B	-43.35 (-10.93)	3.66	3.34
	PD	OB_C	-32.08 (+0.34)	6.00	3.34
	TW		-45.96 (-13.54)	0.00	3.34
	TW-PD		-49.90 (-17.48)	1.35	3.37
4	S		-25.38 (0.00)	0.00	3.60
	PD_I	OV_A	-45.80 (-20.42)	1.66	3.31
	PD_{II}	OV_A	-44.50 (-19.11)	2.94	3.23
	PD_I	OV_B	-33.15 (-7.77)	5.37	3.24
	PD_{II}	OV_B	-13.76 (11.62)	9.64	3.33
	PD	OB_A	-44.43 (-19.04)	1.45	3.34
	PD	OB_B	-37.27 (-11.88)	3.62	3.30
	PD_C	OB_C	-28.10 (-2.72)	5.80	3.30
	TW		-36.85 (-11.47)	0.00	3.45
	TW-PD		-43.66 (-18.28)	1.43	3.35
			M06-2X/6-311+g*		
1	S		-15.09 (0.00)	0.00	3.55
	PD_A	OV	-24.94 (-9.85)	1.58	3.30
	PD_B	OV	-22.99 (-7.90)	2.79	3.24
	PD_A	OB	-24.25 (-9.16)	1.40	3.34
	PD_B	OB	-18.08 (-3.00)	3.51	3.33
	TW		-24.15 (-9.06)	0.00	3.37
	TW-PD		-22.41 (-7.32)	1.94	3.35
2	S		-29.78 (0.00)	0.00	3.54
	PD_A	OV	-47.12 (-17.34)	1.57	3.29
	PD_B	OV	-44.47 (-14.69)	2.71	3.26
	PD_C	OV	-29.21 (+0.57)	5.59	3.26
	PD_A	OB	-46.06 (-16.28)	1.39	3.33
	PD_B	OB	-40.12 (-10.34)	3.67	3.29

	PD_C	OB	-27.42 (+2.37)	5.99	3.30
	TW		-42.98 (-13.20)	0.00	3.38
			M06-2X/6-311+g(2d,p)		
1	S		-11.17 (0.00)	0.00	3.67
	PD_A	OV	-19.84 (-8.67)	1.60	3.36
	PD_B	OV	-18.25 (-7.08)	2.86	3.28
	PD_A	OB	-19.06 (-7.89)	1.41	3.36
	PD_B	OB	-13.96 (-2.79)	3.56	3.36
	TW		-19.07 (-7.90)	0.00	3.39
	TW-PD		-17.67 (-6.50)	3.38	2.00
			M06-2X/TZVP		
1	S		-8.51 (0.00)	0.00	3.66
	PD_A	OV	-18.45 (-9.94)	1.61	3.29
	PD_B	OV	-17.16 (-8.65)	2.89	3.23
	PD_A	OB	-17.43 (-8.92)	1.40	3.34
	PD_B	OB	-12.80 (-4.29)	3.61	3.33
	TW		-17.33 (-8.82)	0.00	3.37
	TW-PD		-15.93 (-7.42)	2.07	3.34

Unconstrained optimization of 1**.** The four PD minima of **1** (PD_I-OV_A, PD_{II}-OV_A, PD-OB_a, PD-OB_B) were optimized unconstrained in C_1 symmetry at the M06-2X/TZVP level. The PD-OV minima optimized to structures similar to the constrained structures with minor distortions to the monomers, typically involving slight out-of-plane bending of the hydrogen atoms. Fully optimized PD_I-OV_A and PD_{II}-OV_A (coordinates below) are 0.1 and 0.4 kcal/mol lower in energy than the constrained dimers. MOs have the same character as the constrained dimers with no greater than 0.012 eV difference in the MO energies versus the constrained dimer MOs. PD-OB_A and PD-OB_B optimize to the lower energy PD_I-OV_A and PD_{II}-OV_A conformations, respectively, consistent with experimentally observed packing for **1** (see main text).

Unconstrained optimized coordinates of **1** (PD_I-OV_A)

6	-2.654422	-0.001554	0.789730
6	-1.990481	1.232001	1.041231
6	-1.988003	-1.233580	1.042239
6	-0.650508	1.233098	1.520802
6	-0.648075	-1.231595	1.521918
6	0.020807	0.001521	1.761124
6	-3.971239	-0.003079	0.290488
6	-2.655146	2.450844	0.806363
6	-2.650206	-2.453948	0.808343
6	0.010862	2.452998	1.760222
6	0.015689	-2.449976	1.762478
6	1.349316	0.003050	2.228222
6	-4.616058	1.241222	0.052088
6	-4.613540	-1.248874	0.053058
6	-1.968428	3.668353	1.063190
6	-3.984763	2.422183	0.306342
6	-3.979871	-2.428354	0.308253
6	-1.961070	-3.669861	1.066201
6	1.353818	2.425939	2.224432
6	-0.684659	3.668397	1.520438
6	-0.677352	-3.666961	1.523611
6	1.358557	-2.419851	2.226799

6	2.000803	-1.239818	2.452582
6	1.998336	1.247379	2.451475
1	-5.630741	1.234087	-0.329588
1	-5.628226	-1.244078	-0.328648
1	-2.486717	4.603613	0.884430
1	-4.491517	3.363560	0.126986
1	-4.484721	-3.370888	0.129604
1	-2.477452	-4.606303	0.888107
1	1.864113	3.368725	2.386352
1	-0.167714	4.603612	1.702646
1	-0.158554	-4.600987	1.706631
1	1.870616	-3.361490	2.389803
1	3.029312	-1.231516	2.794141
1	3.026864	1.241415	2.793016
6	-0.020693	-0.001585	-1.761409
6	0.648046	1.231565	-1.522001
6	0.650745	-1.233131	-1.521274
6	1.987936	1.233614	-1.042229
6	1.990642	-1.231973	-1.041505
6	2.654421	0.001615	-0.789765
6	-1.349256	-0.003170	-2.228331
6	-0.015863	2.449909	-1.762345
6	-0.010522	-2.453064	-1.760814
6	2.649950	2.454017	-0.807984
6	2.655317	-2.450784	-0.806485
6	3.971152	0.003210	-0.290290
6	-2.000901	1.239652	-2.452468
6	-1.998188	-1.247538	-2.451675
6	0.677038	3.666929	-1.523250
6	-1.358738	2.419720	-2.226629
6	-1.353465	-2.426071	-2.225077
6	0.685014	-3.668431	-1.520913
6	3.979554	2.428488	-0.307737
6	1.960695	3.669895	-1.065683
6	1.968697	-3.668323	-1.063411
6	3.984846	-2.422051	-0.306229
6	4.616024	-1.241057	-0.051845
6	4.613303	1.249034	-0.052619
1	-3.029439	1.231284	-2.793934
1	-3.026750	-1.241619	-2.793117
1	0.158140	4.600927	-1.706133
1	-1.870890	3.361333	-2.389495
1	-1.863594	-3.368887	-2.387334
1	0.168145	-4.603672	-1.703196
1	4.484278	3.371047	-0.128862
1	2.476939	4.606364	-0.887329
1	2.486980	-4.603560	-0.884510
1	4.491617	-3.363401	-0.126780
1	5.630642	-1.233866	0.330002
1	5.627936	1.244282	0.329229

Unconstrained optimized coordinates of **1** (PD_{II}-OV_{A})

6	-3.244362	0.000002	-0.449530
6	-2.591504	-1.232827	-0.731967
6	-2.591497	1.232830	-0.731959
6	-1.270720	-1.232424	-1.262309
6	-1.270715	1.232423	-1.262307
6	-0.606998	-0.000002	-1.517367
6	-4.526973	0.000004	0.133244
6	-3.234326	-2.451880	-0.445718
6	-3.234310	2.451885	-0.445698
6	-0.610715	-2.450477	-1.510475
6	-0.610705	2.450473	-1.510470
6	0.713507	-0.000004	-2.006398
6	-5.152863	-1.244739	0.416310
6	-5.152855	1.244750	0.416321
6	-2.551283	-3.668719	-0.717377
6	-4.532131	-2.424724	0.132628
6	-4.532114	2.424733	0.132650
6	-2.551260	3.668721	-0.717352
6	0.721042	-2.424249	-2.005135
6	-1.288453	-3.667664	-1.229321
6	-1.288433	3.667663	-1.229304
6	0.721050	2.424241	-2.005138
6	1.361026	1.243994	-2.236848
6	1.361023	-1.244004	-2.236845
1	-6.141050	-1.238843	0.861459
1	-6.141041	1.238857	0.861471
1	-3.054159	-4.604456	-0.500974
1	-5.022291	-3.366583	0.350870
1	-5.022267	3.366594	0.350899
1	-3.054129	4.604460	-0.500940
1	1.230492	-3.365757	-2.173887
1	-0.773403	-4.601794	-1.422715
1	-0.773378	4.601790	-1.422694
1	1.230503	3.365746	-2.173890
1	2.387780	1.236391	-2.586976
1	2.387777	-1.236406	-2.586972
6	0.606913	0.000001	1.517162
6	1.270678	-1.232420	1.262198
6	1.270677	1.232421	1.262191
6	2.591402	-1.232833	0.731706
6	2.591402	1.232832	0.731700
6	3.244275	-0.000001	0.449305
6	-0.713550	0.000002	2.006330
6	0.610793	-2.450476	1.510664
6	0.610790	2.450479	1.510645
6	3.234329	-2.451891	0.445729
6	3.234329	2.451889	0.445717
6	4.526764	-0.000003	-0.133737
6	-1.360943	-1.244011	2.237077
6	-1.360947	1.244017	2.237063
6	1.288606	-3.667667	1.229709
6	-0.720917	-2.424249	2.005446
6	-0.720923	2.424254	2.005420

6	1.288602	3.667668	1.229682
6	4.532024	-2.424733	-0.132869
6	2.551405	-3.668729	0.717685
6	2.551403	3.668728	0.717664
6	4.532024	2.424728	-0.132879
6	5.152643	1.244744	-0.416819
6	5.152642	-1.244751	-0.416815
1	-2.387639	-1.236463	2.587372
1	-2.387643	1.236470	2.587356
1	0.773644	-4.601798	1.423331
1	-1.230262	-3.365760	2.174493
1	-1.230271	3.365765	2.174456
1	0.773638	4.601800	1.423295
1	5.022218	-3.366592	-0.351037
1	3.054338	-4.604470	0.501434
1	3.054336	4.604468	0.501407
1	5.022218	3.366585	-0.351052
1	6.140734	1.238855	-0.862179
1	6.140734	-1.238864	-0.862175