Electric Field Promotes Pentacene Dimerization in Thin Film Transistors

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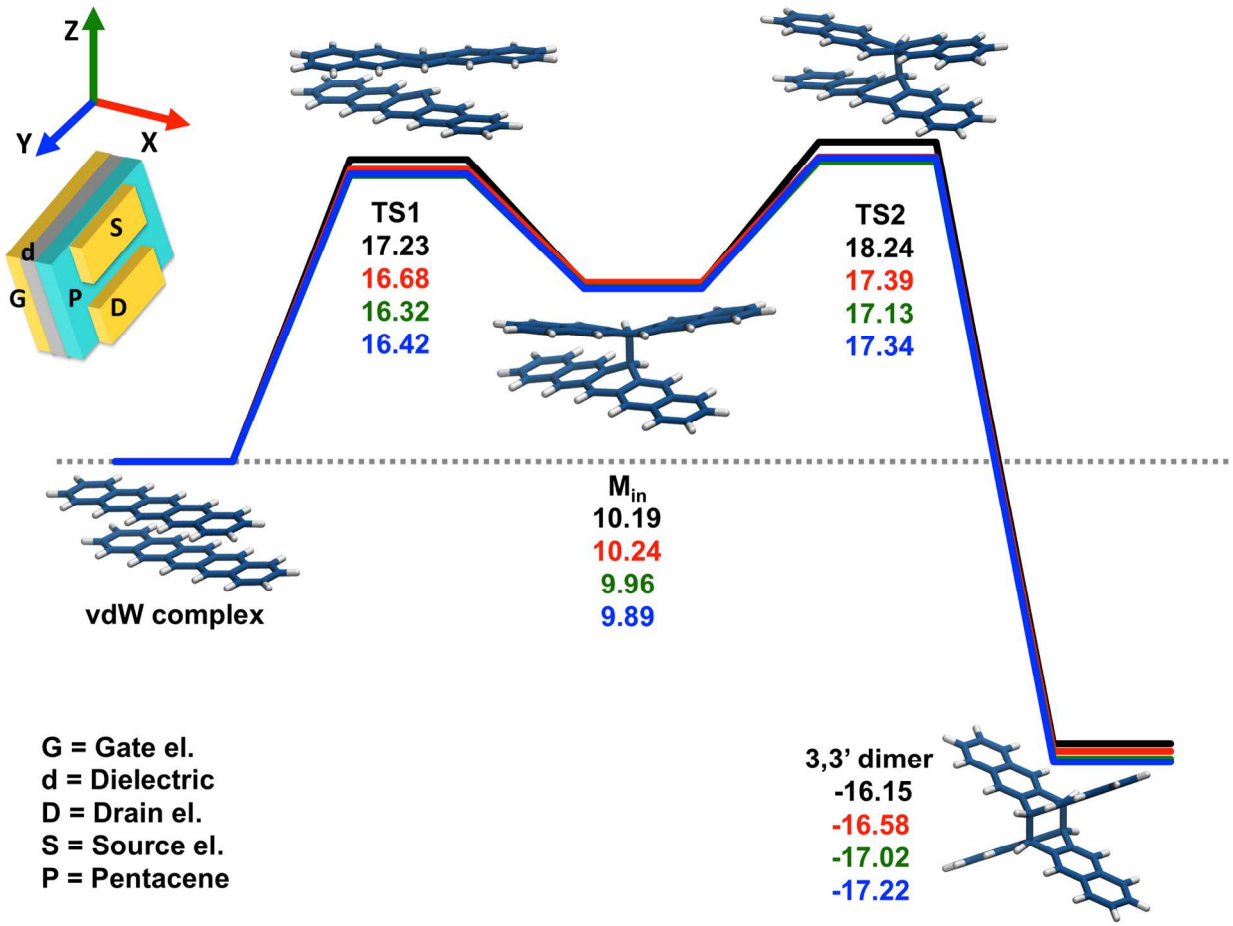

Figure S1. Pentacene dimerization pathway in the absence (black) and the presence of electric fields of 1 V/nm. X (red) corresponds to the long molecular axis, Y (green) to the direction of the sp^3 bonds, and Z (blue) to the short molecular axis. The numbers correspond to the relative energies (with ZPVE) of each species compared to the van der Waals complex, in kcal mol^{-1}, in the same color code.

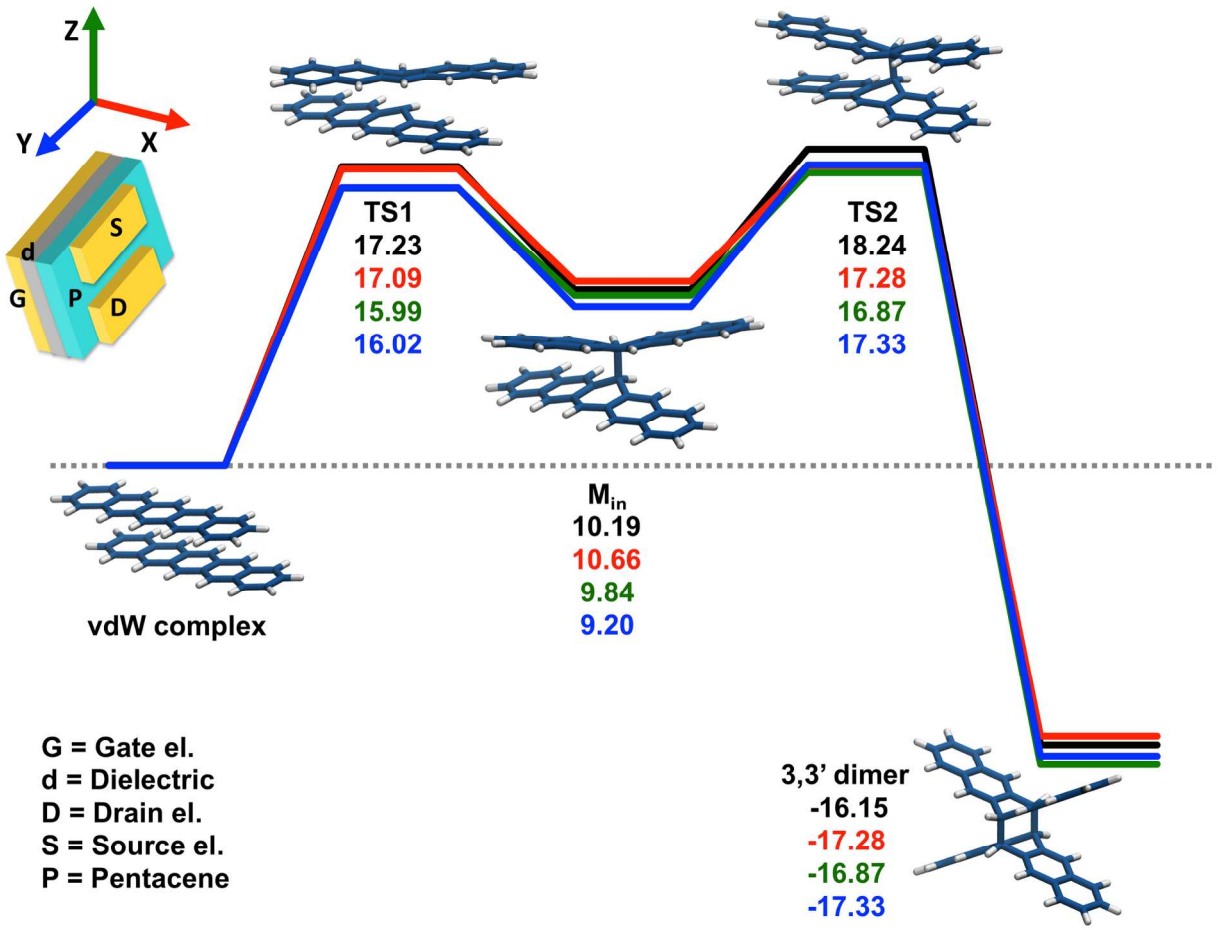

Figure S2. Pentacene dimerization pathway in the absence (black) and the presence of electric fields of 2V/nm. X (red) corresponds to the long molecular axis, Y (green) to the direction of the sp^3 bonds, and Z (blue) to the short molecular axis. The numbers correspond to the relative energies (with ZPVE) of each species compared to the van der Waals complex, in kcal mol^{-1}, in the same color code.

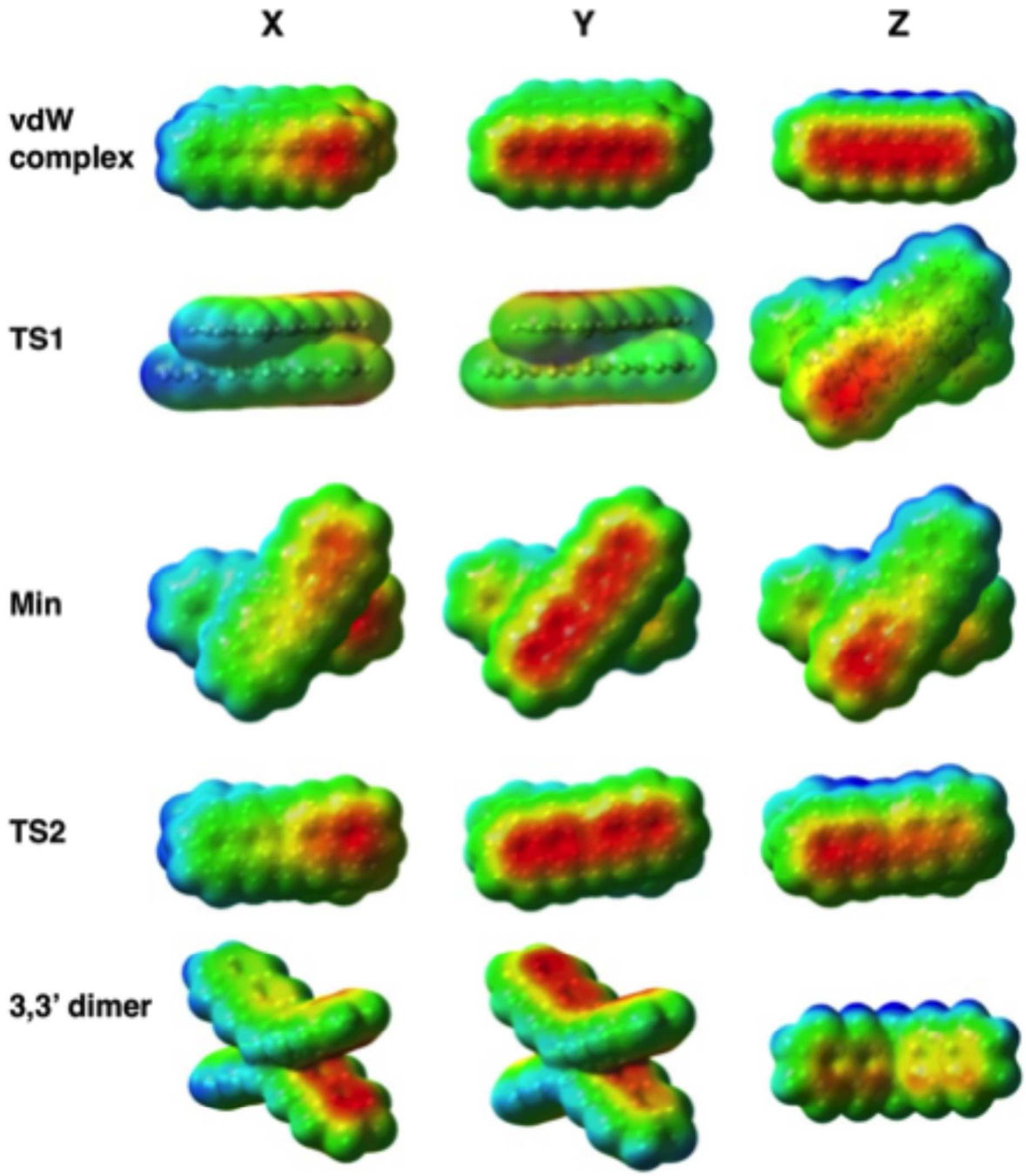

Figure S3. Electrostatic potential maps for all stationary points optimized with an electric field of 3 V/nm along X, Y and Z. In the color code, blue indicates positively charged areas.

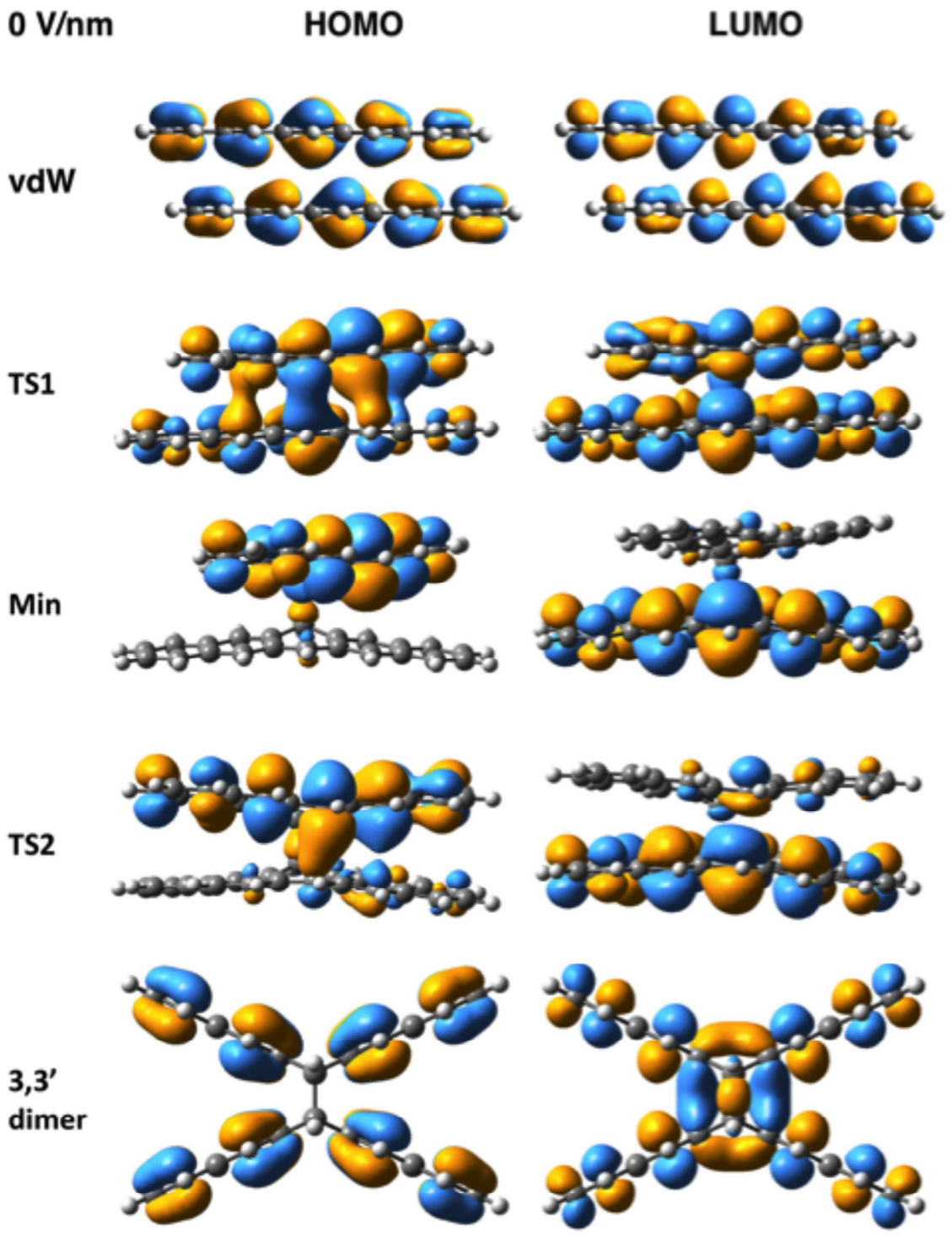

Figure S4. HOMO and LUMO orbitals for all stationary points optimized without an applied electric field.

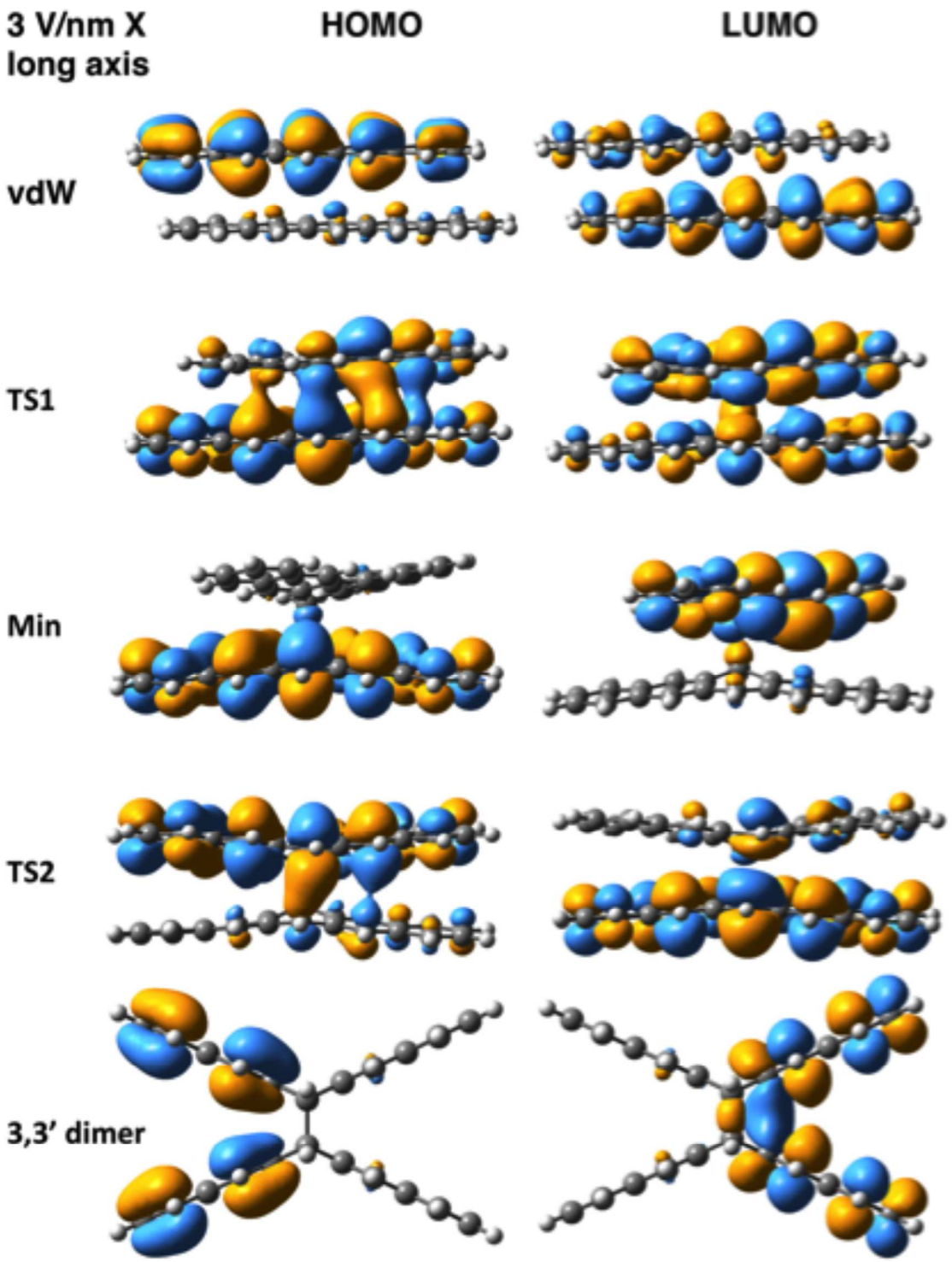

Figure S5. HOMO and LUMO orbitals for all stationary points optimized with an electric field of 3V/nm along X.

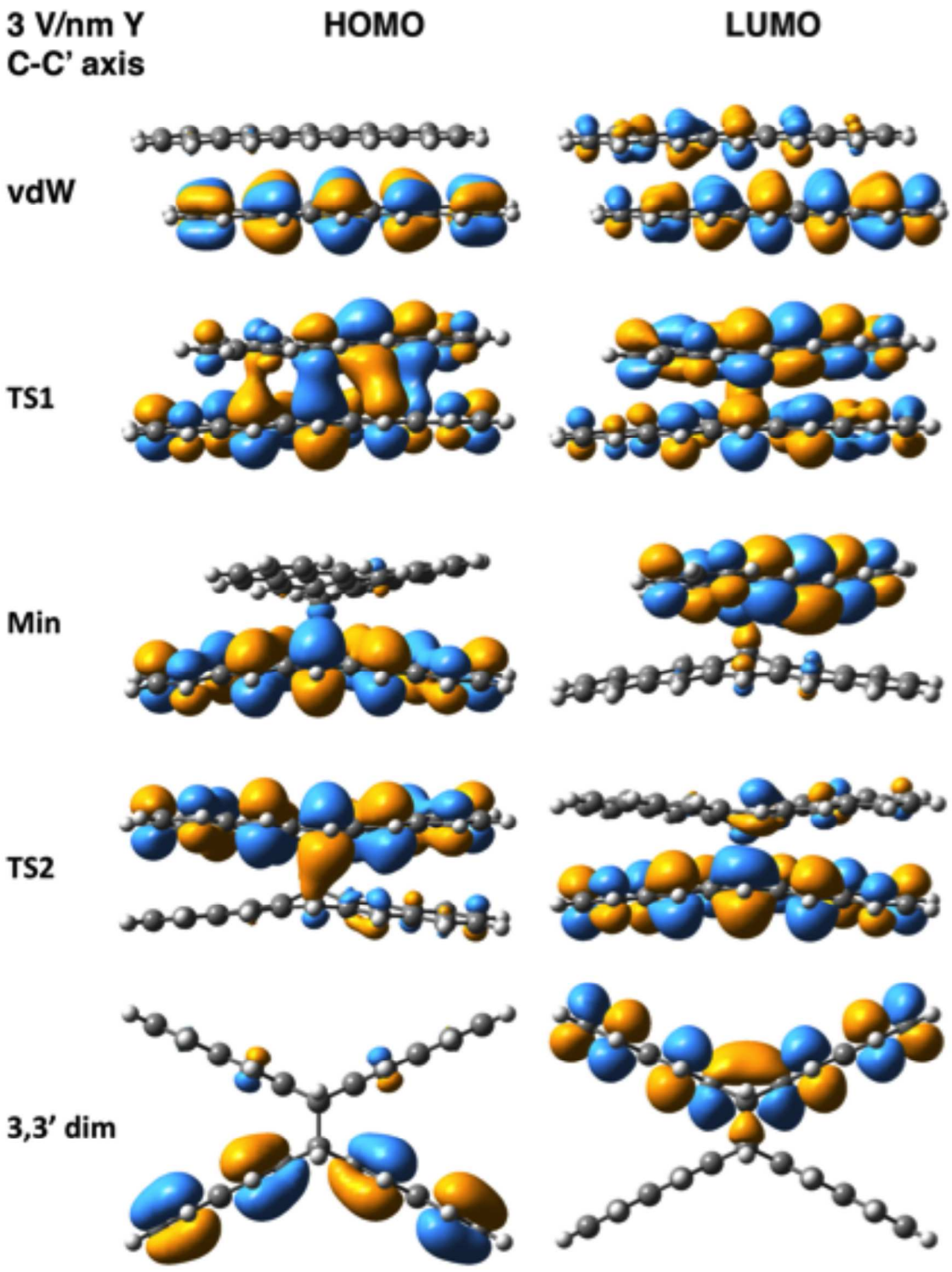

Figure S6. HOMO and LUMO orbitals for all stationary points optimized with an electric field of 3V/nm along Y.

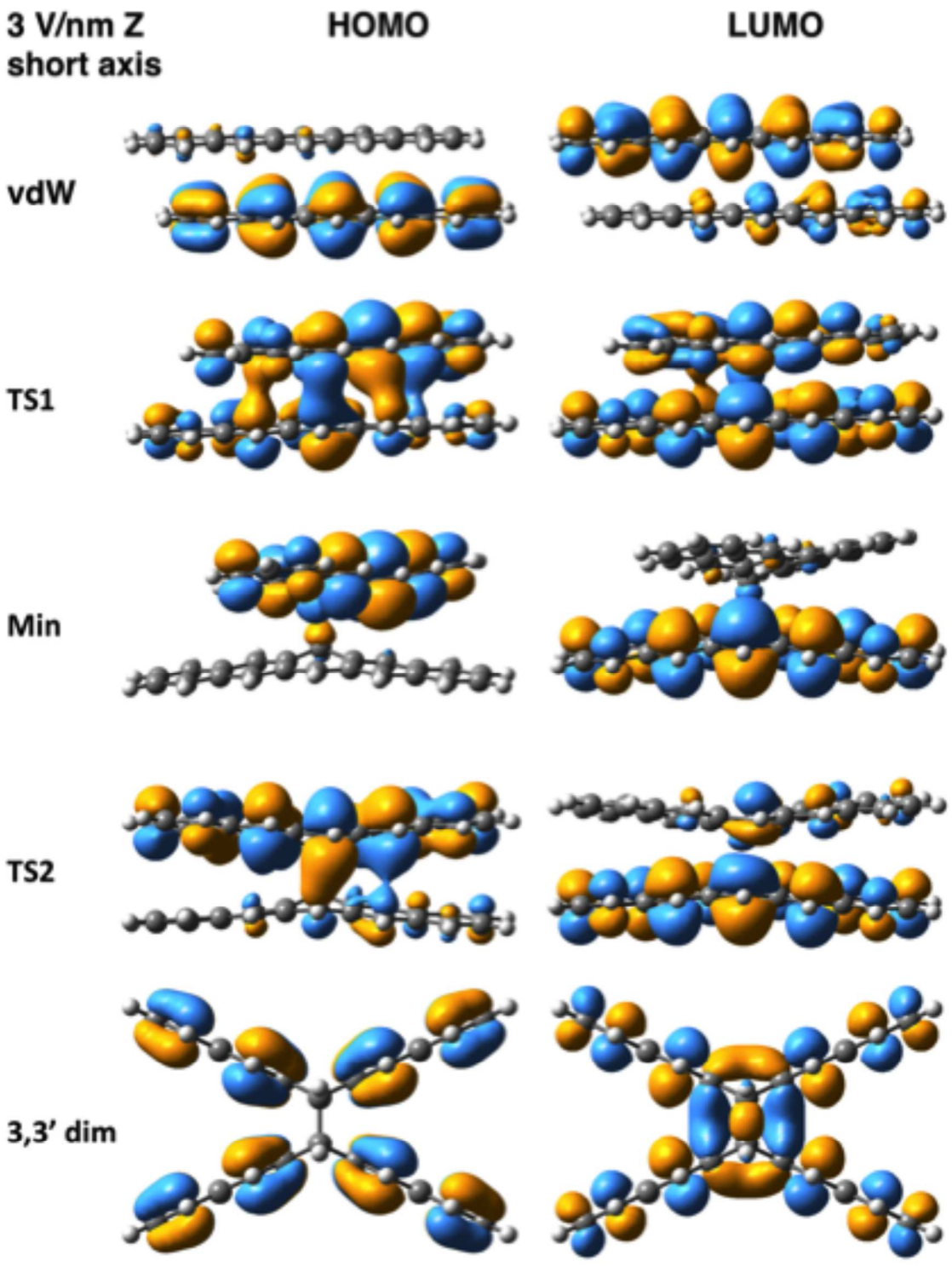

Figure S7. HOMO and LUMO orbitals for all stationary points optimized with an electric field of 3V/nm along Z.

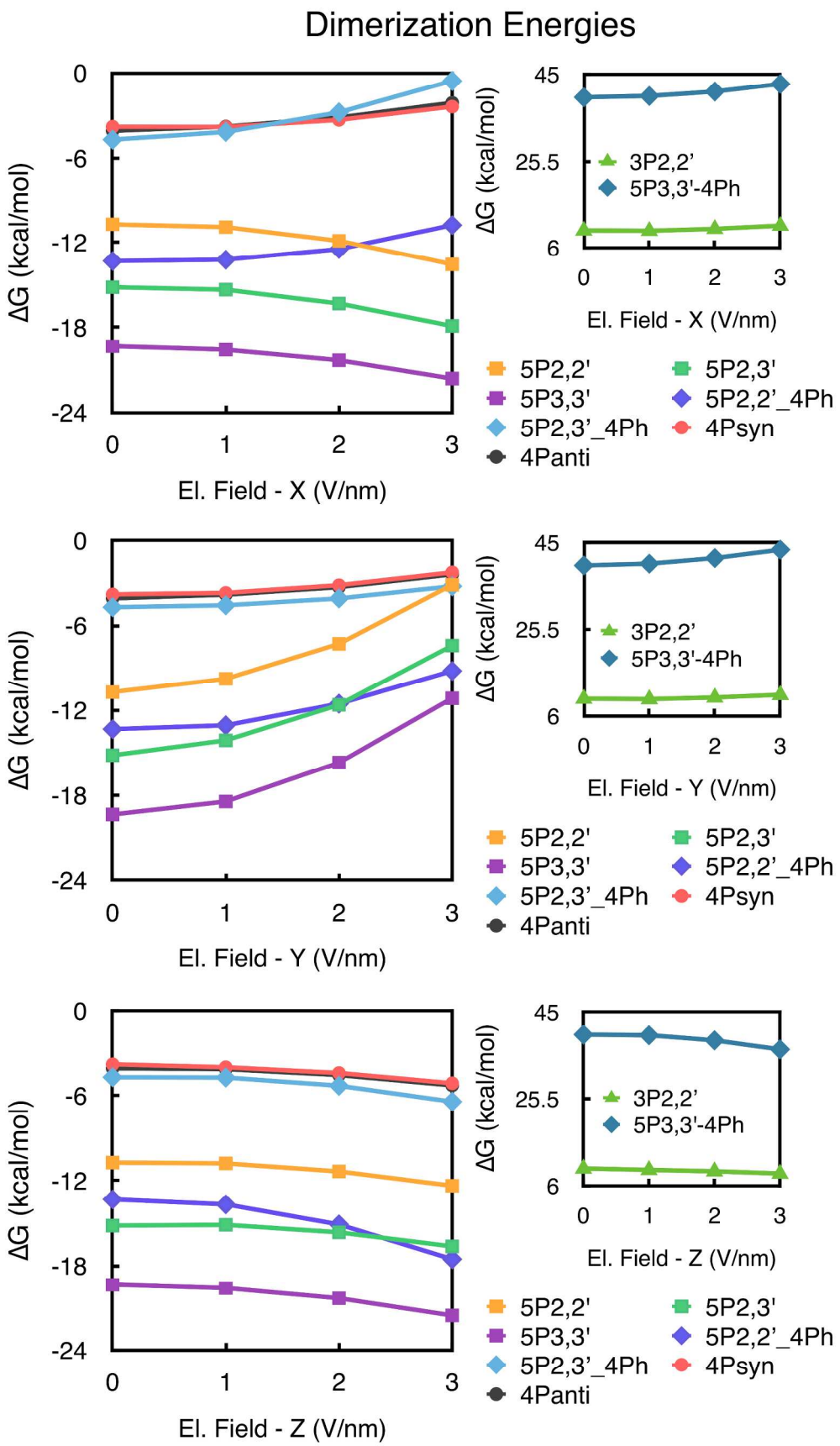
Dimerization Energies
ΔG (kcal/mol)
0
-6
-12
-18
-24
0
1
2
3
El. Field - X (V/nm)
El. Field - Y (V/nm)
El. Field - Z (V/nm)
45
25.5
6
3P2,2'
5P3,3'-4Ph
5P2,2'
5P2,3'
5P3,3'
5P2,2'_4Ph
5P2,3'_4Ph
4Psyn
4Panti

Figure S8. Gibbs free energies of dimerization with electric fields for an acene series including: anthracene (3P2,2', smaller graphs on the right); tetracene syn and anti dimers (4Panti and 4Psyn, with circles), pentacene dimers (5P3,3', 5P2,3' and 5P2,2', with squares) and its tetraphenyl substituted analogues (5P2,3'_4Ph and 5P2,2'_4Ph, with diamonds).

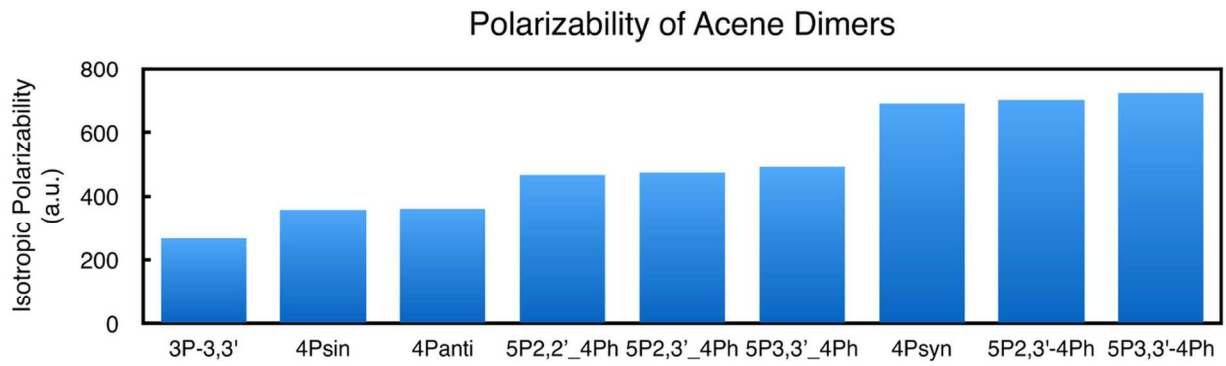

Figure S9. Polarizabilities (in $Bohr^3$) of all acene dimers under study.

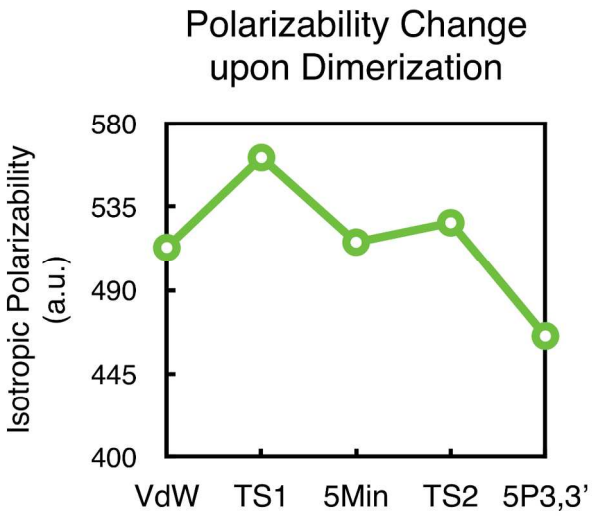

Figure S10. Polarizabilities of reaction intermediates and product for pentacene 3,3' cycloaddition.

Table S1. C-C' bond length (in Å) and C-C-C'-C' dihedral angle (in degrees) for the transition states (TS1 and TS2), the intermediate M_{in} and the 3,3'-dimer.

Electric Field (V/nm)[a]		**TS1**		**Min**		**TS2**		**3,3'-dimer**	
		Bond	Dihedral	Bond	Dihedral	Bond	Dihedral	Bond	Dihedral
	1	2.039	43.05	1.616	58.40	1.656	13.33	1.607	0.00
X	2	2.039	42.96	1.616	58.13	1.657	13.19	1.608	0.00
	3	2.039	42.81	1.618	57.64	1.658	13.13	1.609	0.00
	1	2.037	43.03	1.616	58.43	1.656	13.38	1.607	0.04
Y	2	2.034	42.94	1.616	58.23	1.657	13.84	1.607	0.08
	3	2.018	42.76	1.618	57.84	1.658	15.40	1.607	0.12
	1	2.041	43.25	1.616	58.71	1.656	13.50	1.607	0.00
Z	2	2.043	43.60	1.616	59.21	1.656	13.71	1.607	0.00
	3	2.047	44.25	1.616	59.84	1.656	13.91	1.607	0.00

[a] X corresponds to the pentacene long axis, Y to the direction of the sp^3 bonds, and Z to the short axis.

Table S2. Absolute energies, Gibbs free energies calculated at 298 K (in atomic units), zero-point corrections (in kcal/mol) and spin contamination (<S^2>) for all optimized geometries at level (U)M06-2X/6-31G*.

	Electric Field (V/nm)		E (a.u.)	ZPVE (kcal/mol)	G (a.u.)	<S^2>
vdW complex		*0*	*-1692.90401882*	*364.166*	*-1692.382405*	-
		1	-1692.90603058	365.048	-1692.382657	-
	X	2	-1692.91126781	364.970	-1692.387980	-
		3	-1692.92002713	364.837	-1692.396880	-
		1	-1692.90465211	365.062	-1692.381253	-
	Y	2	-1692.90574595	364.896	-1692.382752	-
		3	-1692.90757691	364.590	-1692.385363	-
		1	-1692.90503584	365.064	-1692.381644	-
	Z	2	-1692.90728062	365.035	-1692.383913	-
		3	-1692.91102421	364.988	-1692.387692	-
TS1		*0*	*-1692.87663427*	*364.214*	*-1692.354715*	*0.21*
		1	-1692.87812354	364.212	-1692.356167	0.21
	X	2	-1692.88275320	364.170	-1692.360820	0.21
		3	-1692.89054662	364.086	-1692.368703	0.22
		1	-1692.87722717	364.172	-1692.355409	0.19
	Y	2	-1692.87902529	364.119	-1692.357405	0.15
		3	-1692.88205057	364.606	-1692.359357	0.00
		1	-1692.87741052	364.144	-1692.355723	0.23
	Z	2	-1692.88014302	364.029	-1692.358868	0.25
		3	-1692.88485372	363.871	-1692.364266	0.28
M_{in}		*0*	*1692.88828983*	*364.489*	*-1692.307439*	*0.99*

		1	-1692.88967854	365.032	-1692.368520	1.02
	X	2	-1692.89422386	364.933	-1692.373251	1.02
		3	-1692.90106997	364.781	-1692.380433	1.01
		1	-1692.88873604	365.037	-1692.367594	1.02
	Y	2	-1692.89017444	364.969	-1692.369217	1.02
		3	-1692.89236876	364.871	-1692.371699	1.00
		1	-1692.88928359	365.072	-1692.368040	1.03
	Z	2	-1692.89265960	365.060	-1692.371409	1.03
		3	-1692.89778205	365.034	-1692.376556	1.03
TS2		*0*	*-1692.87668002*	*365.253*	*-1692.350676*	*0.73*
		1	-1692.87782154	364.733	-1692.353177	0.70
	X	2	-1692.88324849	364.669	-1692.358695	0.68
		3	-1692.89138400	364.628	-1692.366820	0.66
		1	-1692.87666588	364.635	-1692.352324	0.70
	Y	2	-1692.87839354	364.605	-1692.353841	0.75
		3	-1692.88089800	364.350	-1692.357166	0.84
		1	-1692.87683887	364.711	-1692.352250	0.70
	Z	2	-1692.87910229	364.682	-1692.354556	0.70
		3	-1692.88248700	364.630	-1692.358028	0.70
5P3.3'		*0*	*-1692.93645034*	*368.368*	*-1692.408772*	-
		1	-1692.93770937	368.351	-1692.410034	-
	X	2	-1692.94176420	368.462	-1692.413836	-
		3	-1692.94782956	368.184	-1692.420250	-
		1	-1692.93707522	368.388	-1692.409369	-
	Y	2	-1692.93909529	368.527	-1692.411174	-
		3	-1692.94214016	368.490	-1692.414293	-
	Z	1	-1692.93715683	368.004	-1692.409492	-

		2	-1692.93927639	368.325	-1692.411663	-
		3	-1692.94280977	368.264	-1692.415287	-
5P2,3'		*0*	*-1692.92930840*	368.077	-1692.40212	-
		1	-1692.93770937	368.251	-1692.403275	-
	X	2	-1692.94176420	368.191	-1692.407440	-
		3	-1692.94782956	368.073	-1692.414311	-
		1	-1692.93707522	368.250	-1692.402498	-
	Y	2	-1692.93909529	368.214	-1692.404688	-
		3	-1692.94214016	368.154	-1692.408340	-
		1	-1692.93715683	368.277	-1692.402378	-
	Z	2	-1692.93927639	368.322	-1692.404236	-
		3	-1692.94280977	368.346	-1692.407483	-
		-1	-1692.93056331	368.266	-1692.403357	-
	X	-2	-1692.93365887	368.193	-1692.406572	-
		-3	-1692.93869850	368.078	-1692.411800	-
		-1	-1692.93025346	368.274	-1692.403026	-
	Y	-2	-1692.93304921	368.215	-1692.405935	-
		-3	-1692.93780946	368.106	-1692.410910	-
		-1	-1692.93010715	368.271	-1692.402896	-
	Z	-2	-1692.93222031	368.221	-1692.405103	-
		-3	-1692.93574596	368.138	-1692.408787	-
5P2,2'		*0*	-1692.92219613	368.077	-1692.40212	-
		1	-1692.92350348	368.251	-1692.403275	-
	X	2	-1692.92762673	368.191	-1692.407440	-
		3	-1692.93452684	368.073	-1692.414311	-
	Y	1	-1692.92285349	368.250	-1692.402498	-
		2	-1692.92501866	368.214	-1692.404688	-

		3	-1692.92862823	368.154	-1692.408340	-
		1	-1692.92277691	368.277	-1692.402378	-
	Z	2	-1692.92471789	368.322	-1692.404236	-
		3	-1692.92797308	368.346	-1692.407483	-
5P3,3'_4Ph		*0*	-2616.68511928	368.077	-2615.849541	-
	X	1	-2616.68669197	368.251	-2615.851230	-
		2	-2616.69142117	368.191	-2615.856208	-
		3	-2616.69931803	368.073	-2615.864569	-
	Y	1	-2616.68607909	368.250	-2615.850573	-
		2	-2616.68896350	368.214	-2615.853664	-
		3	-2616.69378614	368.154	-2615.859295	-
		1	-2616.68643025	368.277	-2615.850907	-
	Z	2	-2616.69036500	368.322	-2615.854996	-
		3	-2616.69692924	368.346	-2615.861816	-
5P2,3'_4Ph		*0*	-2616.753348	573.100	-2615.920475	-
		1	-2616.754634	573.077	-2615.921764	-
	X	2	-2616.759002	573.013	-2615.926138	-
		3	-2616.766473	572.892	-2615.933688	-
		1	-2616.75475679	573.075	-2615.921921	-
	Y	2	-2616.75898219	573.002	-2615.926261	-
		3	-2616.76602930	572.876	-2615.933518	-
		1	-2616.75449607	573.066	-2615.921638	-
	Z	2	-2616.75758646	573.067	-2615.924822	-
		3	-2616.76266658	573.015	-2615.930205	-
	X	-1	-2616.75514619	573.092	-2615.922223	-
		-2	-2616.76003794	573.054	-2615.927048	-

		-3	-2616.76804607	572.970	-2615.935000	-
		-1	-2616.75475675	573.075	-2615.921921	-
	Y	-2	-2616.75898212	573.003	-2615.926261	-
		-3	-2616.76602920	572.876	-2615.933518	-
		-1	-2616.75412852	573.114	-2615.921412	-
	Z	-2	-2616.75684967	573.030	-2615.924754	-
		-3	-2616.76157559	572.912	-2615.929943	-
5P2,2'_4Ph		*0*	-2616.76412316	573.612	-2615.934215	-
	X	1	-2616.76583097	573.542	-2615.936228	-
		2	-2616.77089417	573.422	-2615.941585	-
		3	-2616.77936997	573.337	-2615.949957	-
		1	-2616.76501969	573.547	-2615.935449	-
	Y	2	-2616.76764183	573.498	-2615.938138	-
		3	-2616.77202309	573.377	-2615.943070	-
		1	-2616.76561549	573.564	-2615.935903	-
	Z	2	-2616.77002370	573.483	-2615.940418	-
		3	-2616.77737845	573.356	-2615.947903	-
4P_syn		*0*	-1385.77004910	309.221	-1385.329645	-
		1	-1385.77125042	309.216	-1385.330842	-
	X	2	-1385.77427633	309.175	-1385.333904	-
		3	-1385.77913358	309.093	-1385.338866	-
		-1	-1385.77067428	309.199	-1385.330290	-
		-2	-1385.77313533	309.152	-1385.332772	-
		-3	-1385.77744653	309.074	-1385.337154	-
		1	-1385.77063182	309.210	-1385.330244	-
	Y	2	-1385.77238012	309.180	-1385.332037	-
		3	-1385.77529578	309.133	-1385.335027	-

		1	-1385.77054410	309.232	-1385.330133	-
	Z	2	-1385.77203527	309.264	-1385.331599	-
		3	-1385.77454180	309.296	-1385.334091	-
4P_anti		*0*	-1385.77027179	309.221	-1385.330090	-
	X	1	-1385.77117079	309.199	-1385.330796	-
		2	-1385.77398360	309.152	-1385.333648	-
		3	-1385.77868126	309.074	-1385.338440	-
	Y	1	-1385.77081838	309.216	-1385.330446	-
		2	-1385.77257215	309.175	-1385.332250	-
		3	-1385.77549529	309.093	-1385.335252	-
	Z	1	-1385.77072641	309.210	-1385.330339	-
		2	-1385.77220640	309.180	-1385.331822	-
		3	-1385.77468394	309.133	-1385.334326	-
3P2,2'		*0*	-1078.60326189	250.051	-1078.250122	-
	X	1	-1078.60386808	250.041	-1078.250747	-
		2	-1078.60568734	250.007	-1078.252627	-
		3	-1078.60872235	249.949	-1078.255767	-
	Y	1	-1078.60371763	250.046	-1078.250588	-
		2	-1078.60509348	250.020	-1078.252003	-
		3	-1078.60738413	249.982	-1078.254353	-
		1	-1078.60362538	250.056	-1078.250486	-
	Z	2	-1078.60471673	250.067	-1078.251585	-
		3	-1078.60653936	250.081	-1078.253434	-

a) X corresponds to the molecule's long axis, Y to the direction of the sp^3 bonds, and Z to the short axis.

Table S3. Isotropic polarizabilities and dipole moments (Debye) of intermediates and dimers (optimized geometries at level (U)M06-2X/6-31G*).

	Electric Field (V/nm)		μ_X (Debye)	μ_Y (Debye)	μ_Z (Debye)	$\lvert\mu\rvert$ (Debye)	α (Bohr^3)
vdW complex		*0*	*0.00*	*0.00*	*0.00*	*0.00*	*512.9*
		1	-4.66	0.02	0.13	4.67	-
	X	2	-9.35	0.04	0.27	9.36	-
		3	-14.09	0.07	0.42	14.10	-
		1	0.02	-0.97	0.04	0.98	-
	Y	2	0.03	-1.95	0.07	1.96	-
		3	0.05	-2.95	0.11	2.95	-
		1	0.13	0.04	2.00	2.01	-
	Z	2	0.27	0.07	4.00	4.01	-
		3	0.40	0.10	6.01	6.03	-
TS1		*0*	*-12.56*	*-0.94*	*2.60*	*12.86*	*561.4*
		1	-4.09	-0.30	1.03	4.23	-
	X	2	-8.30	-0.61	1.81	8.52	-
		3	-12.56	-0.94	2.60	12.86	-
		1	-0.20	-1.59	0.39	1.65	-
	Y	2	-0.50	-3.23	0.53	3.31	-
		3	-0.82	-4.99	0.71	5.11	-
		1	0.87	0.13	-2.34	2.50	-
	Z	2	1.62	0.25	-4.97	5.24	-
		3	2.36	0.37	-7.64	8.01	-
M_{in}		*0*	*-0.01*	*0.01*	*-0.09*	*0.09*	*515.8*
	X	1	-3.75	-0.16	0.73	3.83	-

		2	-7.81	-0.35	1.38	7.94	-
		3	-11.54	-0.51	1.99	11.72	-
		1	-0.11	-1.18	0.21	1.21	-
	Y	2	-0.31	-2.48	0.29	2.52	-
		3	-0.49	-3.73	0.37	3.78	-
		1	0.66	0.10	-2.76	2.84	-
	Z	2	1.27	0.19	-5.83	5.97	-
		3	1.81	0.27	-8.65	8.84	-
TS2		*0*	*0.01*	*-0.01*	*0.03*	*0.03*	*526.3*
		1	-4.50	-0.01	0.27	4.51	-
	X	2	-9.30	-0.05	0.54	9.31	-
		3	-13.70	-0.08	0.80	13.72	-
		1	-0.04	-1.44	0.03	1.44	-
	Y	2	-0.08	-2.94	0.06	2.94	-
		3	-0.14	-4.10	0.10	4.11	-
		1	0.26	0.04	0.88	0.90	-
	Z	2	0.54	0.06	0.88	0.92	-
		3	0.79	0.07	0.69	0.74	-
5P3.3’		*0*	*0.00*	*0.00*	*0.00*	*0.00*	*465.3*
		1	-3.37	0.00	0.00	3.37	-
	X	2	-6.76	0.00	0.00	6.76	-
		3	-10.20	0.00	0.00	10.20	-
		1	0.00	-1.67	0.00	1.67	-
	Y	2	0.00	-3.38	0.00	3.38	-
		3	0.00	-5.14	0.00	5.14	-
	Z	1	0.00	0.00	-1.89	1.89	-
		2	0.00	0.00	-3.78	3.78	-

		3	0.00	0.00	-5.67	5.67	-
5P2,3'		*0*	*-0.27*	*-0.12*	*0.00*	*0.30*	*474.6*
	X	1	-3.78	0.00	0.46	3.80	-
		2	-7.26	0.00	0.93	7.32	-
		3	-10.80	0.00	1.41	10.89	-
	Y	1	-0.30	-1.91	0.00	1.93	-
		2	-0.31	-3.82	0.00	3.83	-
		3	-0.31	-5.73	0.00	5.73	-
		1	0.16	0.00	1.70	1.71	-
	Z	2	0.62	0.00	3.43	3.49	-
		3	1.07	0.00	5.24	5.35	-
5P2,2'		*0*	*0.00*	*0.00*	*0.00*	*0.00*	*492.1*
		1	-3.67	0.00	-0.95	3.79	-
	X	2	-7.37	0.00	-1.90	7.61	-
		3	-11.11	0.00	-2.87	11.47	-
		1	0.00	-1.93	0.00	1.93	-
	Y	2	0.00	-3.86	0.00	3.86	-
		3	0.00	-5.80	0.00	5.80	-
	Z	1	-0.95	0.00	-1.73	1.97	-
		2	-1.90	0.00	-3.47	3.96	
		3	-2.87	0.00	-5.25	5.98	-
5P3,3'_4Ph		*0*	*0.00*	*0.00*	*0.00*	*0.00*	*690.4*
	X	1	-4.21	0.00	0.00	4.21	-
		2	-8.44	0.00	0.00	8.44	-
		3	-12.69	0.00	0.00	12.69	-
	Y	1	0.00	-2.57	0.01	2.57	-
		2	0.00	-5.15	0.03	5.15	-

		3	0.00	-7.76	0.04	7.76	-
	Z	1	0.01	0.02	-3.51	3.51	-
		2	0.01	0.03	-7.02	7.02	
		3	0.01	0.04	-10.54	10.54	-
5P2,3'_4Ph		*0*	-4.21	0.00	0.00	4.21	*700.8*
		1	-8.44	0.00	0.00	8.44	-
	X	2	-12.69	0.00	0.00	12.69	-
		3	0.00	-2.57	0.01	2.57	-
		1	0.00	-5.15	0.03	5.15	-
	Y	2	0.00	-7.76	0.04	7.76	-
		3	0.01	0.02	-3.51	3.51	-
		1	0.01	0.03	-7.02	7.02	-
	Z	2	0.01	0.04	-10.54	10.54	-
		3	-4.21	0.00	0.00	4.21	-
		-1	-8.44	0.00	0.00	8.44	-
	X	-2	-12.69	0.00	0.00	12.69	-
		-3	0.00	-2.57	0.01	2.57	-
		-1	0.00	-5.15	0.03	5.15	-
	Y	-2	0.00	-7.76	0.04	7.76	-
		-3	0.01	0.02	-3.51	3.51	-
		-1	0.01	0.03	-7.02	7.02	-
	Z	-2	0.01	0.04	-10.54	10.54	-
		-3	-4.21	0.00	0.00	4.21	-
5P2,2'_4Ph		*0*	-8.44	0.00	0.00	8.44	*721.3*
	X	1	-12.69	0.00	0.00	12.69	-
		2	0.00	-2.57	0.01	2.57	-
		3	0.00	-5.15	0.03	5.15	-

		1	0.00	-7.76	0.04	7.76	-
	Y	2	0.01	0.02	-3.51	3.51	-
		3	0.01	0.03	-7.02	7.02	-
		1	0.01	0.04	-10.54	10.54	-
	Z	2	-4.21	0.00	0.00	4.21	-
		3	-8.44	0.00	0.00	8.44	-
4P_syn		*0*	*-0.39*	*0*	*0*	*0.39*	*357.1*
		1	-2.83	0.00	0.00	2.83	-
	X	2	-5.27	0.00	0.00	5.27	-
		3	-7.73	0.00	0.00	7.73	-
		-1	2.06	0.00	0.00	2.06	-
		-2	4.53	0.00	0.00	4.53	-
		-3	7.01	0.00	0.00	7.01	-
		1	-0.39	-1.56	0.00	1.61	-
	Y	2	-0.39	-3.12	0.00	3.14	-
		3	-0.39	-4.68	0.00	4.70	-
		1	-0.39	0.00	-1.33	1.38	-
	Z	2	-0.39	0.00	-2.67	2.70	-
		3	-0.40	0.00	-4.05	4.07	-
4P_anti		*0*	*0.00*	*0.00*	*0.00*	*0.00*	*361.3*
	X	1	-2.51	0.00	-0.41	2.54	-
		2	-5.02	0.00	-0.82	5.09	-
		3	-7.55	0.00	-1.24	7.65	-
	Y	1	0.00	-1.56	0.00	1.56	-
		2	0.00	-3.13	0.00	3.13	-
		3	0.00	-4.69	0.00	4.69	-
	Z	1	-0.41	0.00	-1.32	1.38	-

		2	-0.82	0.00	-2.64	2.77	-
		3	-1.24	0.00	-3.99	4.18	-
3P2,2'		*0*	*0.00*	*0.00*	*0.00*	*0.00*	*266.0*
	X	1	-1.62	0.00	0.00	1.62	-
		2	-3.25	0.00	0.00	3.25	-
		3	-4.87	0.00	0.00	4.87	-
	Y	1	0.00	-1.22	0.00	1.22	-
		2	0.00	-2.45	0.00	2.45	-
		3	0.00	-3.68	0.00	3.68	-
		1	0.00	0.00	-0.97	0.97	-
	Z	2	0.00	0.00	-1.95	1.95	-
		3	0.00	0.00	-2.93	2.93	-

a) X corresponds to the molecule's long axis, Y to the direction of the sp^3 bonds, and Z to the short axis.