A Systematic Theoretical Study of the Electronic Structures of Porphyrin Dimers: DFT and TD-DFT Calculations on Diporphyrins Linked by Ethane, Ethene, Ethyne, Imine, and Azo Bridges

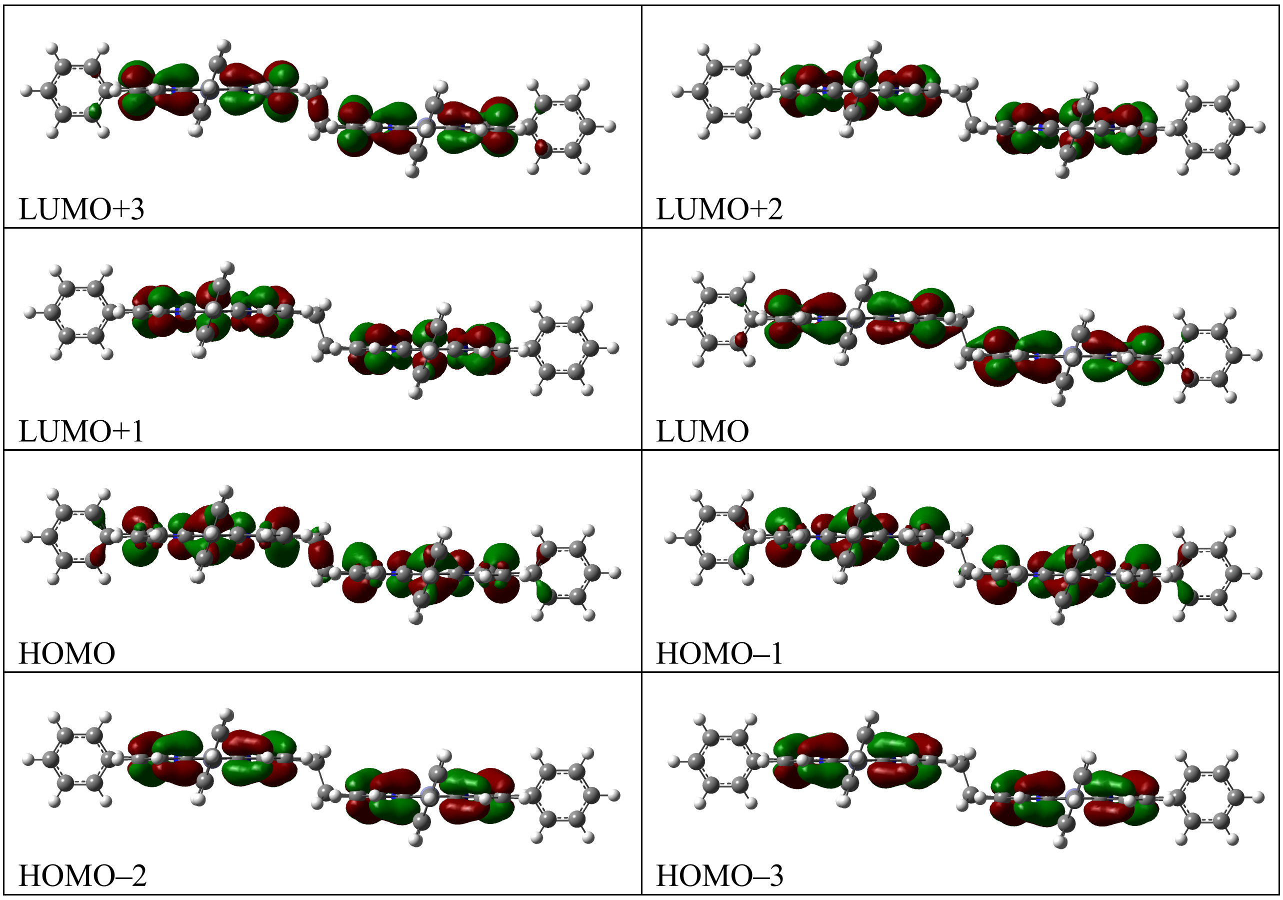
Llew Rintoul, Shannon R. Harper, and Dennis P. Arnold

Supplementary Information

Table of Contents

1. ZnTriPP–CH_2CH_2–ZnTriPP (1)

Figure S1. The eight frontier orbitals of ethane dimer **1**.



LUMO+3

LUMO+2

LUMO+1

LUMO

HOMO

HOMO–1

HOMO–2

HOMO–3

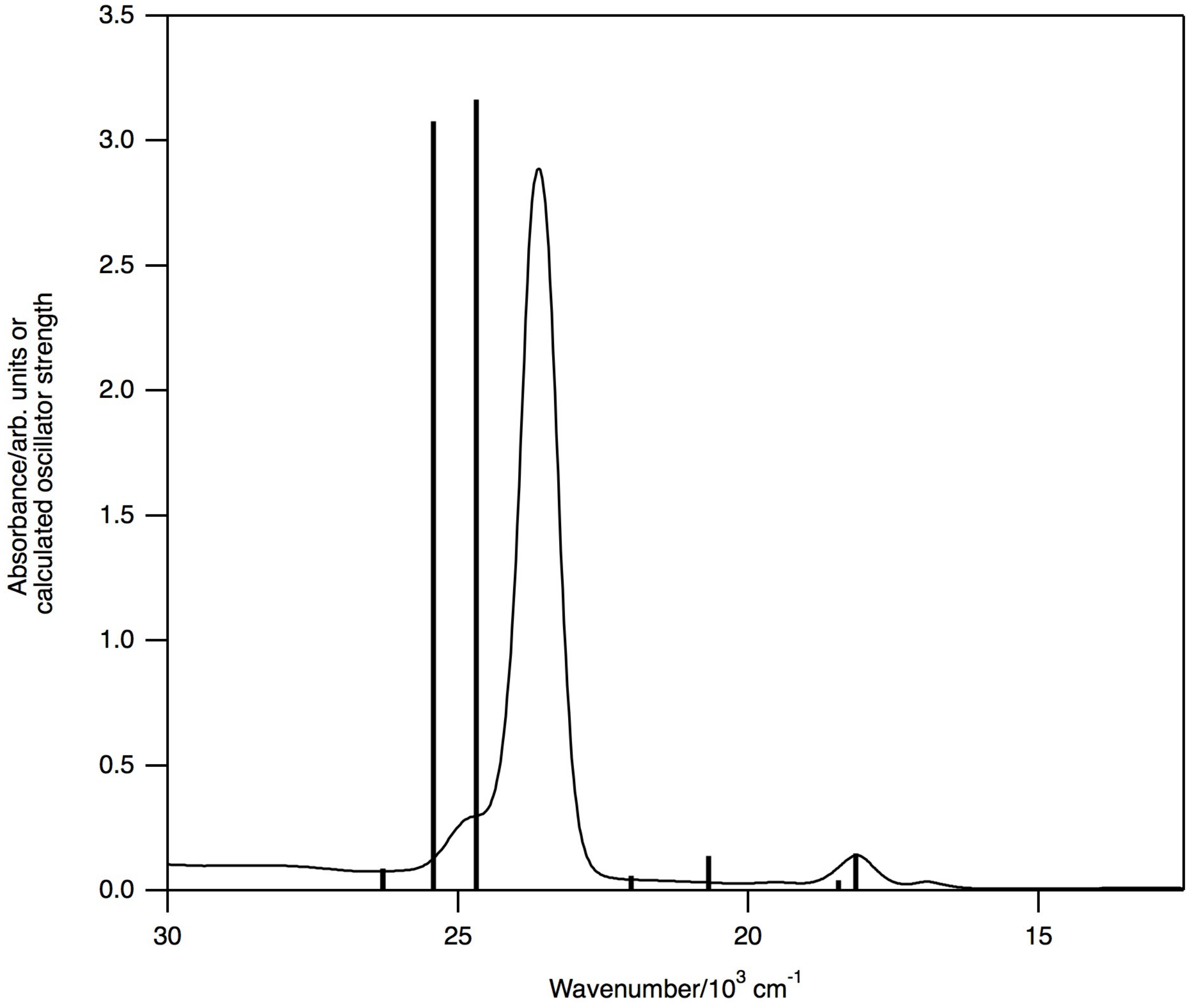
Table S1. The eigenvalues for the eight frontier orbitals of ethane dimer **1**.

Orbital	**Number**	**Symmetry**	**Energy/h**	**Energy/eV**
LUMO+3	321	x_2*	-0.07860	-2.1387846
LUMO+2	320	y_2*	-0.08124	-2.21062164
LUMO+1	319	y_1*	-0.08134	-2.21334274
LUMO	318	x_1*	-0.08406	-2.28735666
HOMO	317	x_1	-0.18322	-4.98559942
HOMO-1	316	x_2	-0.18798	-5.11512378
HOMO-2	315	y_1	-0.19252	-5.23866172
HOMO-3	314	y_2	-0.19292	-5.24954612

Table S2. TD-DFT calculated excitation energies, one-electron transitions and oscillator strengths for selected optical transitions of **1** in toluene ($\lambda \geq 333$ nm, $f \geq 0.05$, contribution ≥10%).

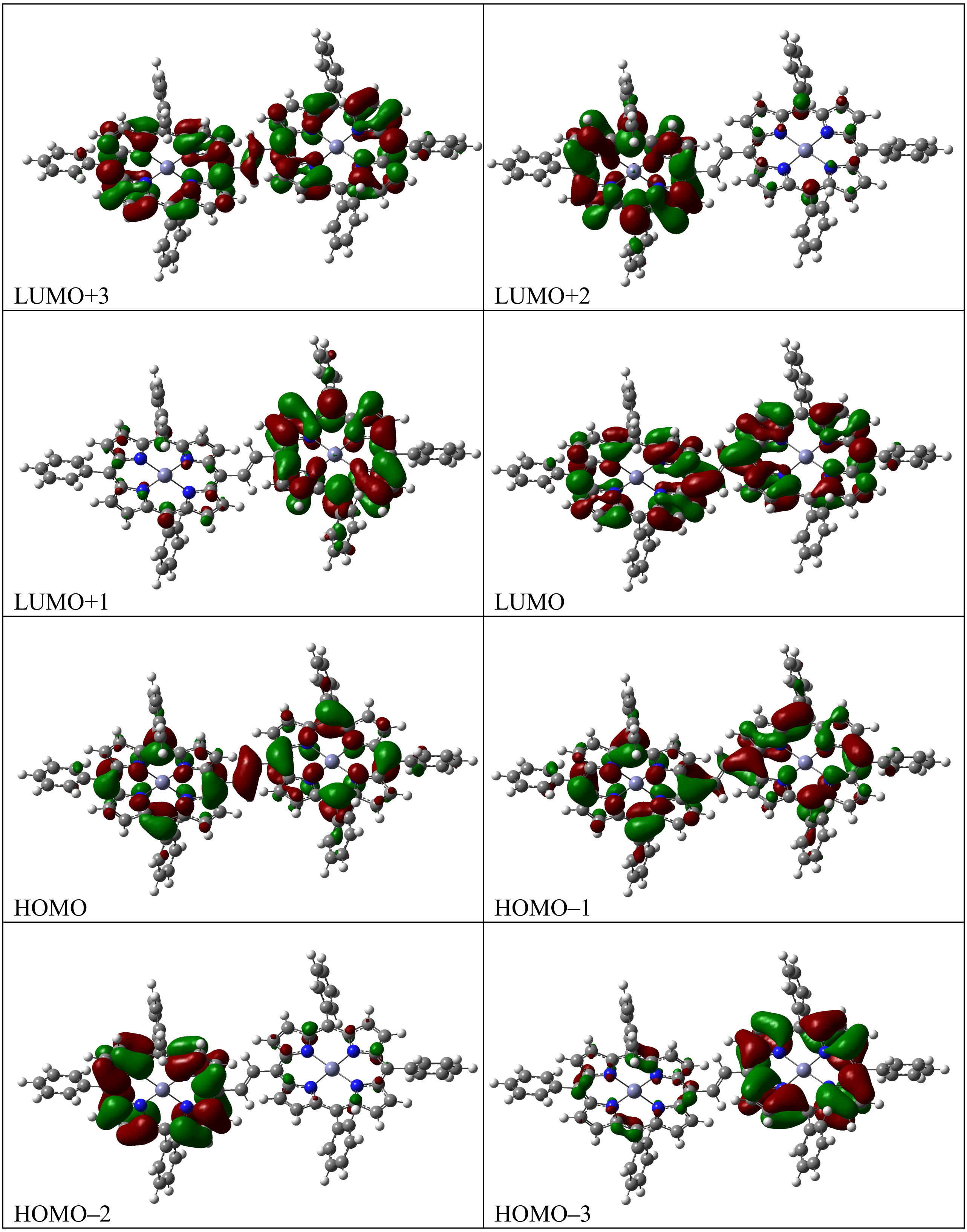
Excited state	**From**	**To**	**Coefficient**	**%**	**eV**	**nm**	**cm^{-1}**	***f***
1	314	320	-0.25642	13	2.2507	551	18153	0.1491
	315	319	-0.26361	14				
	317	318	0.57031	65				
2	314	321	0.25061	13	2.2875	542	18450	0.0406
	315	318	0.36258	26				
	316	320	0.28518	16				
	317	319	0.47092	44				
7	316	320	0.23901	11	2.5651	483	20689	0.1385
	316	321	0.48876	48				
	317	318	-0.32399	21				
10	314	321	-0.48112	46	2.7305	454	22023	0.0579
	315	318	0.50029	50				
13	314	320	0.38854	30	3.0614	405	24692	3.1639
	315	319	0.37184	28				
	316	321	0.40291	32				
15	314	321	0.44402	39	3.1527	393	25428	3.0784
	315	318	0.31731	20				
	316	320	-0.33032	22				
	317	319	-0.27908	16				
20	312	320	0.48851	48	3.2605	380	26297	0.0876
	313	319	0.49697	49				
25	308	318	0.42122	35	3.2605	380	26297	0.0876
	310	321	-0.22227	10				
	311	318	-0.37462	28				
27	306	320	0.26666	14	3.7231	333	30029	0.0538
	307	320	-0.29412	17				
	308	319	0.34391	24				
	310	320	-0.25328	13				
	311	319	-0.30565	19				

Figure S2. Comparison of electronic absorption spectrum for *meso*-2-phenylethylZnTriPP (toluene) and one-electron transitions calculated by TD-DFT for ethane dimer **1** in the same medium (vertical bars). The vertical scales were chosen to make the comparison convenient (see text).



2. ZnTriPP–CH=CH–ZnTriPP (2)

Figure S3. The eight frontier orbitals of the ethene dimer **2** in its twisted minimum-energy conformation.



LUMO+3

LUMO+2

LUMO+1

LUMO

HOMO

HOMO–1

HOMO–2

HOMO–3

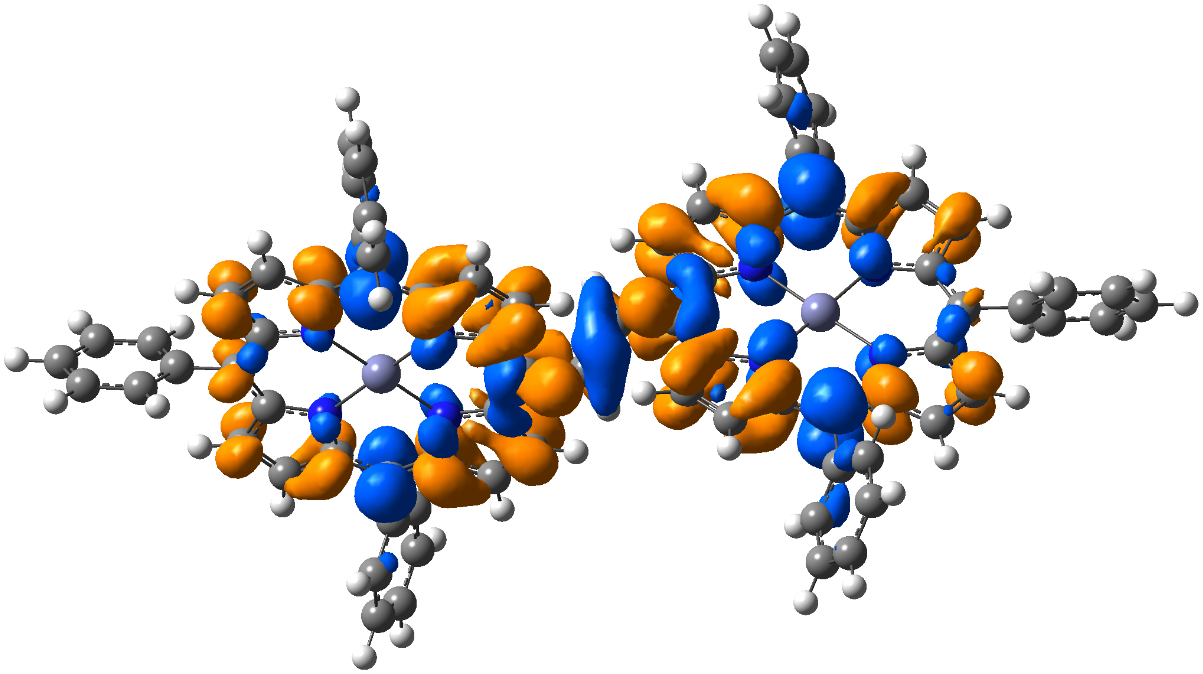
Table S3. The eigenvalues for the eight frontier orbitals of ethene dimer **2**.

Orbital	**Number**	**Symmetry**	**Energy/h**	**Energy/eV**
LUMO+3	320	x_2*	-0.07532	-2.04953252
LUMO+2	319	y_2*	-0.08126	-2.21116586
LUMO+1	318	y_1*	-0.08178	-2.22531558
LUMO	317	x_1*	-0.09154	-2.49089494
HOMO	316	x_1	-0.17670	-4.8081837
HOMO-1	315	x_2	-0.19156	-5.21253916
HOMO-2	314	y_1	-0.19311	-5.25471621
HOMO-3	313	y_2	-0.19340	-5.2626074

Table S4. TD-DFT calculated excitation energies, one-electron transitions and oscillator strengths for selected optical transitions of **2** in toluene ($\lambda \geq 333$ nm, $f \geq 0.05$, contribution ≥10%).

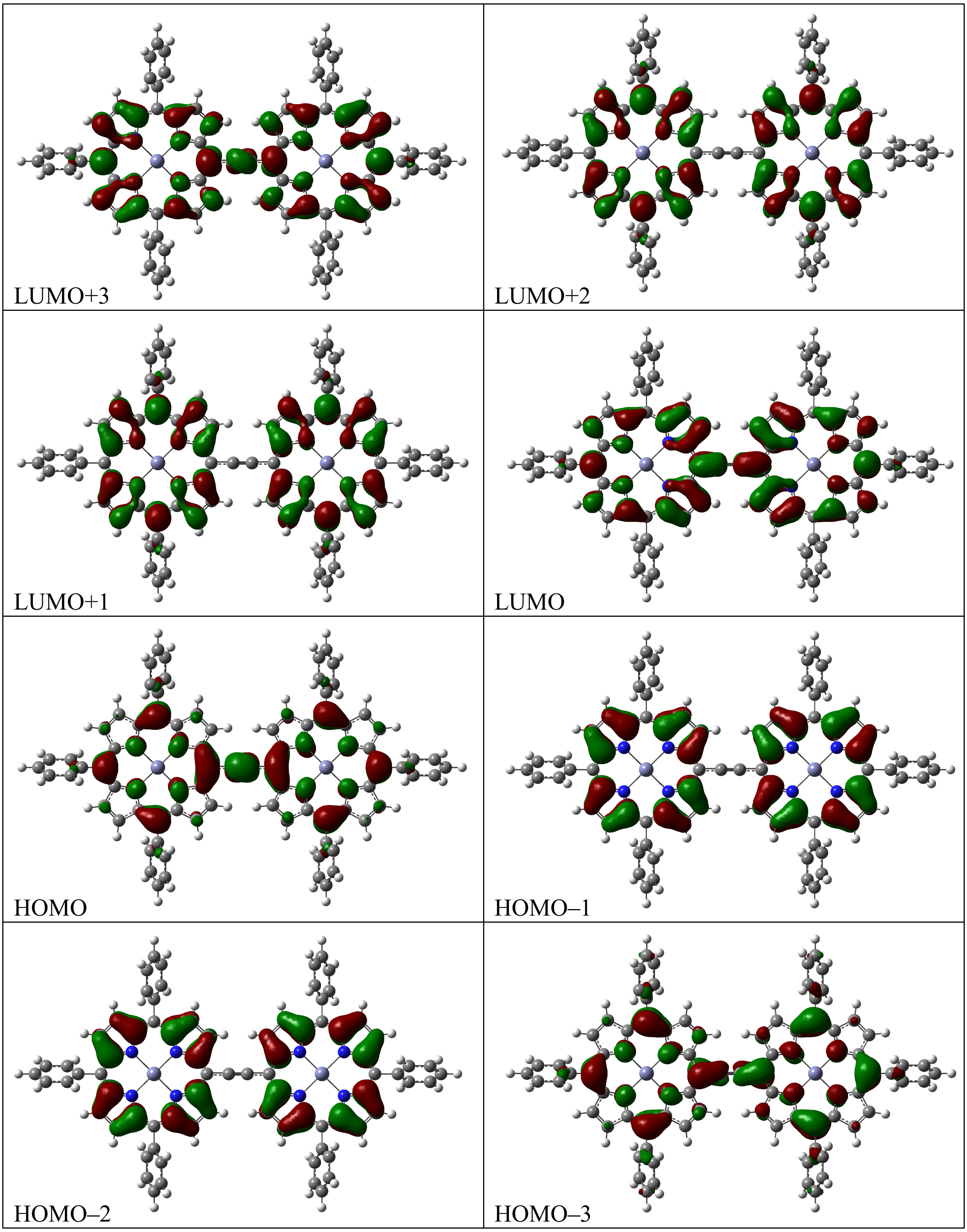
Excited state	**From**	**To**	**Coefficient**	**%**	**eV**	**nm**	**cm^{-1}**	***f***
1	316	317	0.67936	92	1.9477	637	15709	0.9632
6	314	317	0.41818	35	2.5057	495	20210	0.0854
	315	319	-0.32515	21				
	316	319	0.37774	29				
7	313	317	0.41104	34	2.5276	491	20387	0.1002
	315	318	-0.33787	23				
	316	318	-0.34757	24				
8	313	318	0.34357	24	2.6051	476	21011	0.8472
	314	319	-0.36637	27				
	315	320	0.42185	36				
9	313	320	-0.3045	19	2.693	460	21721	0.1174
	314	317	0.28491	16				
	315	318	0.42434	36				
10	313	317	-0.26983	15	2.7044	458	21812	0.0868
	314	320	0.37519	28				
13	313	318	-0.33083	22	3.0532	406	24626	1.5667
	315	320	0.44034	39				
14	313	320	0.4892	48	3.0887	401	24912	1.1142
	315	318	0.26463	14				
15	314	320	0.46363	43	3.1344	396	25281	1.2555
	315	319	-0.29141	17				
16	311	317	-0.31122	19	3.1427	395	25347	0.2418
	312	317	0.31808	20				
	314	319	0.2675	14				
17	311	317	0.23264	11	3.1716	391	25580	0.1601
	312	317	0.54599	60				
	312	320	-0.24822	12				
18	311	317	0.47809	46	3.2517	381	26226	0.0626
	313	318	0.2182	10				
20	311	318	0.63599	81	3.3326	372	26879	0.2153
25	305	317	-0.37119	28	3.5562	349	28682	0.0049
	308	317	0.46585	43				
27	316	321	0.65215	85	3.5905	345	28959	0.0536

Figure S4. Electron density distribution map of the HOMO-LUMO transition for **2** (blue: electron-poor region after transition; orange: electron-rich region after transition)



3. ZnTriPP–CC–ZnTriPP (3)

Figure S5. The eight frontier orbitals of the ethyne dimer **3** in a conformation close to its global minimum energy.



LUMO+3

LUMO+2

LUMO+1

LUMO

HOMO

HOMO–1

HOMO–2

HOMO–3

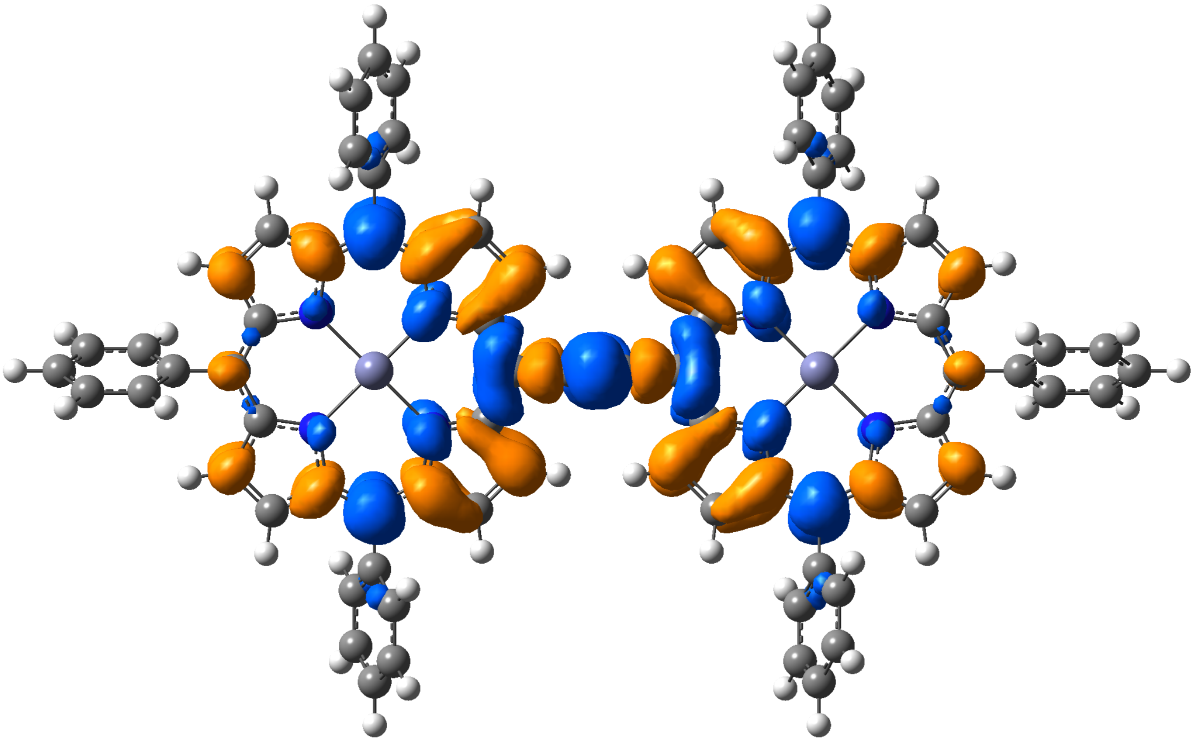
Table S5. The eigenvalues for the eight frontier orbitals of ethyne dimer **3**.

Orbital	**Number**	**Symmetry**	**Energy/h**	**Energy/eV**
LUMO+3	319	x_2*	-0.07724	-2.10177764
LUMO+2	318	y_2*	-0.08261	-2.24790071
LUMO+1	317	y_1*	-0.08274	-2.25143814
LUMO	316	x_1*	-0.09724	-2.64599764
HOMO	315	x_1	-0.17548	-4.77498628
HOMO-1	314	y_1	-0.19474	-5.29907014
HOMO-2	313	y_2	-0.19485	-5.30206335
HOMO-3	312	x_2	-0.19772	-5.38015892

Table S6. TD-DFT calculated excitation energies, one-electron transitions and oscillator strengths for selected optical transitions of **3** in toluene ($\lambda \geq 333$ nm, $f \geq 0.05$, contribution ≥10%).

Excited state	**From**	**To**	**Coefficient**	**%**	**eV**	**nm**	**cm^{-1}**	***f***
1	315	316	0.69046	95	1.801	688	14526	1.3377
7	312	318	0.24558	12	2.4868	499	20057	0.3626
	314	316	0.5253	55				
	315	317	-0.38143	29				
8	312	319	0.37152	28	2.6373	470	21272	1.1893
	313	318	0.3943	31				
	314	317	0.41647	35				
13	309	316	0.22545	10	3.0867	402	24896	0.2917
	310	319	-0.22046	10				
	311	316	0.51261	53				
	312	319	0.31356	20				
15	312	317	0.43013	37	3.1031	400	25028	0.0663
	314	319	0.49616	49				
16	309	316	-0.31854	20	3.1209	397	25171	0.9384
	312	319	0.48724	47				
17	312	318	0.41924	35	3.1522	393	25424	2.4096
	313	319	0.48654	47				
20	309	317	0.26155	14	3.3131	374	26722	0.112
	310	318	0.48871	48				
	311	317	0.41984	35				
21	309	316	0.54433	59	3.3489	370	27011	0.1419
	311	316	-0.3561	25				
27	315	320	0.65025	85	3.5296	351	28468	0.1062

Figure S6. Electron density distribution map of the HOMO-LUMO transition for **3** (blue: electron-poor region after transition; orange: electron-rich region after transition).



4. ZnTriPP–CH=N–ZnTriPP (4)

Figure S7. The eight frontier orbitals of the imine dimer **4** in its twisted minimum-energy conformation.

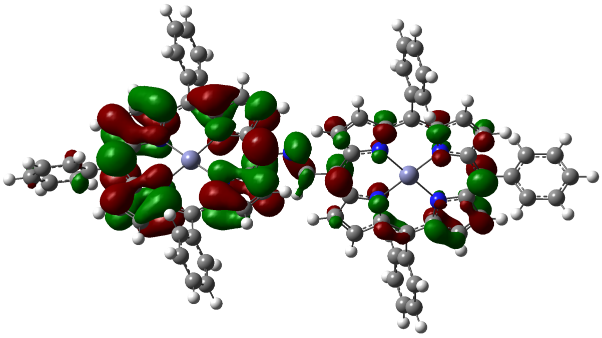
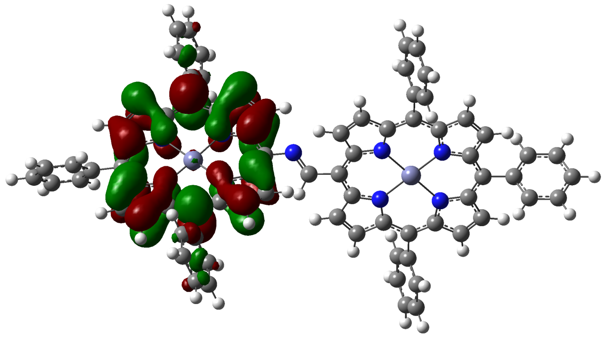
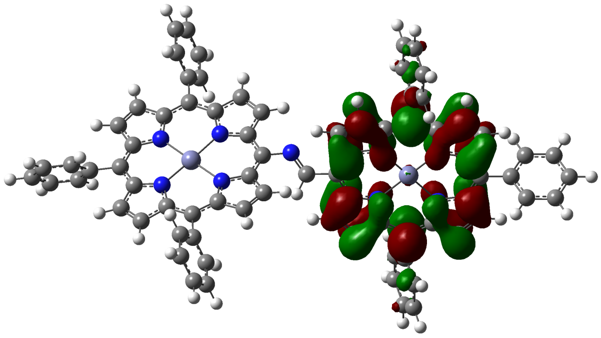
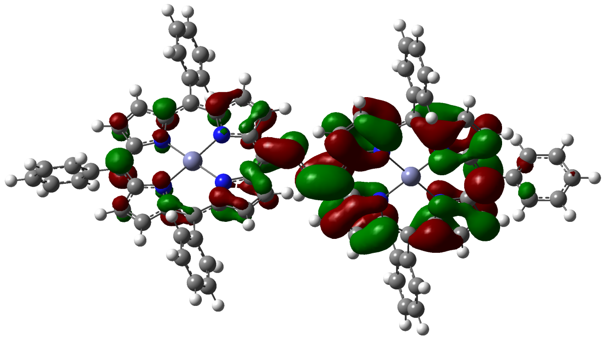
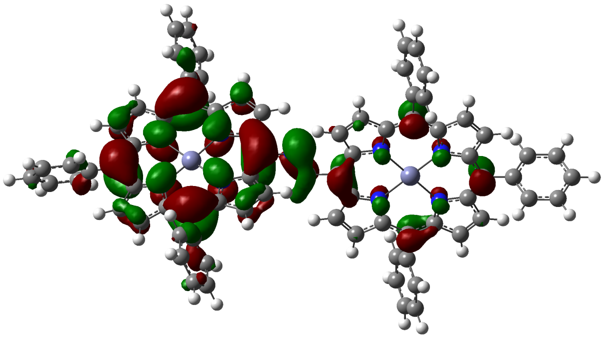
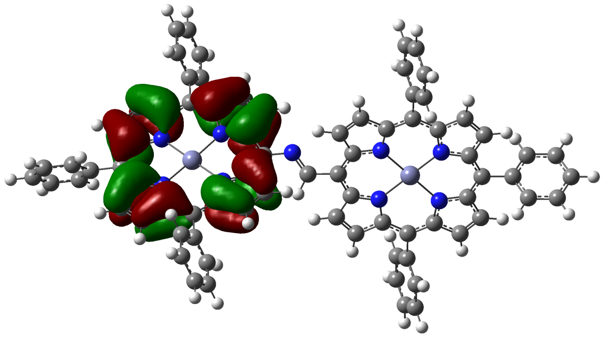
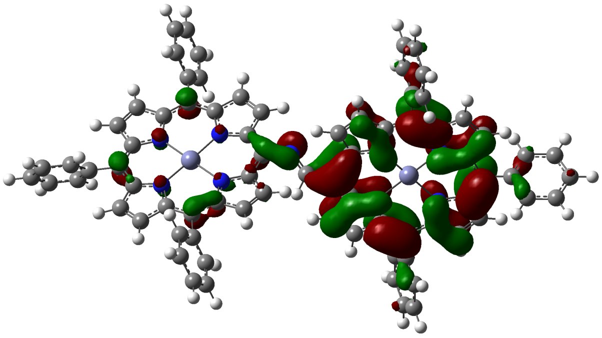
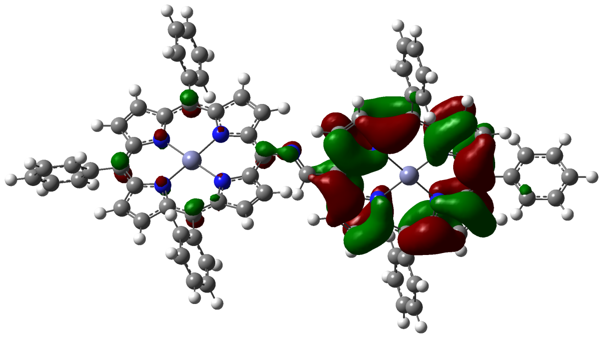
 LUMO+3	 LUMO+2
 LUMO+1	 LUMO
 HOMO	 HOMO–1
 HOMO–2	 HOMO–3

Table S7. The eigenvalues for the eight frontier orbitals of imine dimer **4**.

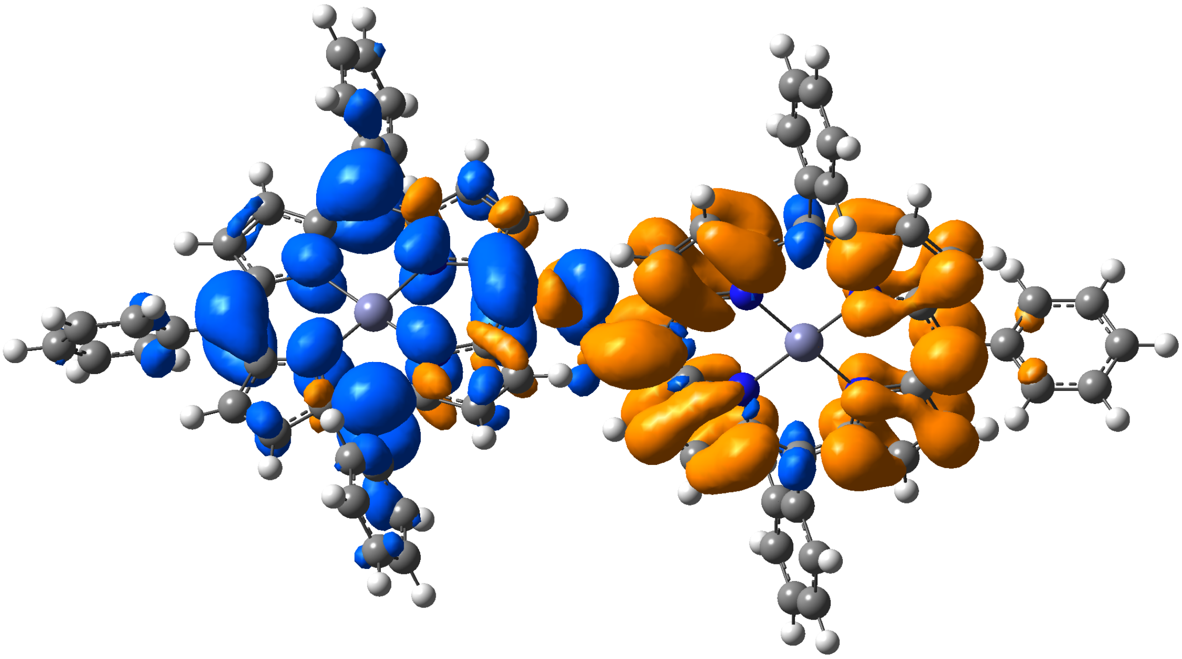
Orbital	**Number**	**Symmetry**	**Energy/h**	**Energy/eV**
LUMO+3	320	x_2*	-0.07464	-2.03102904
LUMO+2	319	y_2*	-0.07957	-2.16517927
LUMO+1	318	y_1*	-0.08447	-2.29851317
LUMO	317	x_1*	-0.09719	-2.64463709
HOMO	316	x_1	-0.17610	-4.7918571
HOMO-1	315	y_1	-0.19135	-5.20682485
HOMO-2	314	x_2	-0.19544	-5.31811784
HOMO-3	313	y_2	-0.19676	-5.35403636

Table S8. TD-DFT calculated excitation energies, one-electron transitions and oscillator strengths for selected optical transitions of **4** in toluene ($\lambda \geq 333$ nm, $f \geq 0.05$, contribution ≥10%).

Excited state	**From**	**To**	**Coefficient**	**%**	**eV**	**nm**	**cm^{-1}**	***f***
1	316	317	0.69443	96	1.797	690	14494	0.8473
4	313	317	0.36381	26	2.2618	548	18243	0.0496
	313	318	0.26341	14				
	314	317	0.47513	45				
	314	318	-0.22149	10				
6	313	317	0.34766	24	2.3671	524	19092	0.0597
	314	317	-0.22075	10				
	314	318	-0.26578	14				
	316	318	0.37233	28				
7	315	317	0.47319	45	2.3865	520	19249	0.1643
	315	320	-0.28345	16				
	316	319	0.41614	35				
9	313	318	0.33296	22	2.7239	455	21970	1.4905
	314	320	-0.31117	19				
	315	319	0.34792	24				
11	313	317	0.27265	15	2.8297	438	22823	0.3441
	313	320	0.32405	21				
	314	318	0.36621	27				
	314	320	-0.28915	17				
14	313	320	0.31614	20	3.0863	402	24892	1.2356
	314	320	0.46937	44				
	315	319	0.26097	14				
15	313	319	-0.22782	10	3.119	398	25157	1.1949
	314	319	-0.21887	10				
	314	320	0.10507	2				
	315	320	0.53618	57				
	316	319	0.26497	14				
16	313	318	-0.23813	11	3.1335	396	25273	1.006
	313	320	0.46753	44				
	314	318	-0.26865	14				
	314	320	-0.25435	13				
18	313	318	-0.28736	17	3.2006	387	25814	0.0582
	314	318	0.24094	12				
	315	319	0.34532	24				
	316	320	-0.29824	18				

25	316	321	0.62957	79	3.4521	359	27843	0.1642

Figure S8. Electron density distribution map of the HOMO-LUMO transition for imine **4** (imino-N on the left-hand ring as in Figure S7 above; blue: electron-poor region after transition; orange: electron-rich region after transition).



5. ZnTriPP–N=N–ZnTriPP (5)

Figure S9. The eight frontier orbitals of azo dimer **5** in its twisted minimum-energy conformation.

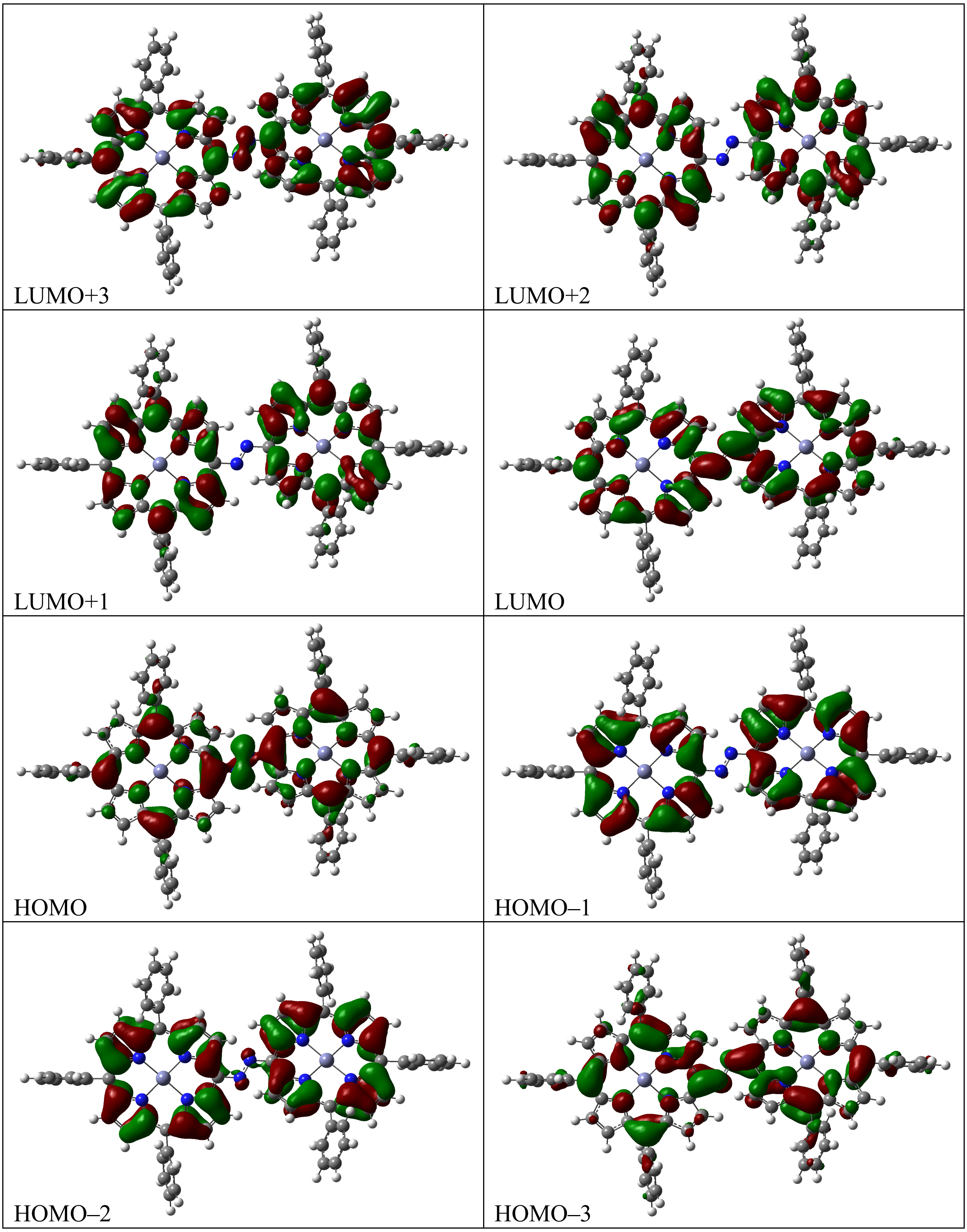

LUMO+3
LUMO+2
LUMO+1
LUMO
HOMO
HOMO–1
HOMO–2
HOMO–3

Table S9. The eigenvalues for the eight frontier orbitals of azo dimer **5**.

Orbital	**Number**	**Symmetry**	**Energy/h**	**Energy/eV**
LUMO+3	320	x_2*	-0.07565	-2.05851215
LUMO+2	319	y_2*	-0.08187	-2.22776457
LUMO+1	318	y_1*	-0.08211	-2.23429521
LUMO	317	x_1*	-0.10557	-2.87266527
HOMO	316	x_1	-0.17552	-4.77607472
HOMO-1	315	y_1	-0.19359	-5.26777749
HOMO-2	314	y_2	-0.19381	-5.27376391
HOMO-3	313	x_2	-0.20011	-5.44519321

Table S10. TD-DFT calculated excitation energies, one-electron transitions and oscillator strengths for selected optical transitions of **5** in toluene ($\lambda \geq 333$ nm, $f \geq 0.05$, contribution ≥10%).

Excited state	**From**	**To**	**Coefficient**	**%**	**eV**	**nm**	**cm^{-1}**	f
1	316	317	0.68996	95	1.5733	788	12690	1.3812
5	312	317	0.48414	47	2.2866	542	18443	0.1768
	316	319	0.41561	35				
7	315	317	-0.36266	26	2.3353	531	18836	0.1053
	316	318	0.55055	61				
8	312	317	0.43234	37	2.3956	518	19322	0.234
	314	317	0.30409	18				
	316	319	-0.38471	30				
9	313	320	-0.28806	17	2.6544	467	21410	1.4333
	314	319	0.40613	33				
	315	318	0.42606	36				
16	308	317	-0.28019	16	3.0821	402	24859	0.2667
	313	319	-0.37029	27				
	314	320	0.44546	40				
17	309	317	-0.31067	19	3.0863	402	24892	0.5214
	313	318	-0.24289	12				
	313	320	0.36638	27				
	315	320	0.28498	16				
	316	321	0.246	12				
18	306	317	0.31888	20	3.1166	398	25137	0.0877
	308	317	0.52039	54				
19	305	317	-0.27317	15	3.1307	396	25251	0.933
	309	317	0.3063	19				
	313	318	-0.31506	20				
	315	320	0.36432	27				
20	305	317	0.45609	42	3.1451	394	25367	0.338
	313	320	-0.33034	22				
	316	321	-0.22849	10				
24	307	317	-0.26264	14	3.2527	381	26234	0.1838
	312	319	0.49322	49				
	316	321	0.25515	13				
26	307	317	0.57991	67	3.2666	380	26347	0.1044
	316	321	0.22261	10				
28	312	319	0.37245	28	3.3104	375	26700	0.5218
	313	320	0.2501	13				

	316	321	-0.35567	25				
30	310	319	0.43944	39	3.3909	366	27349	0.2841
	311	318	0.43761	38				
	312	319	0.25344	13				
31	310	318	0.24543	12	3.4004	365	27427	0.0781
	311	319	0.23938	11				
	312	320	0.56447	64				

Figure S10. Electron density distribution map of the HOMO-LUMO transition for **5** (blue: electron-poor region after transition; orange: electron-rich region after transition).

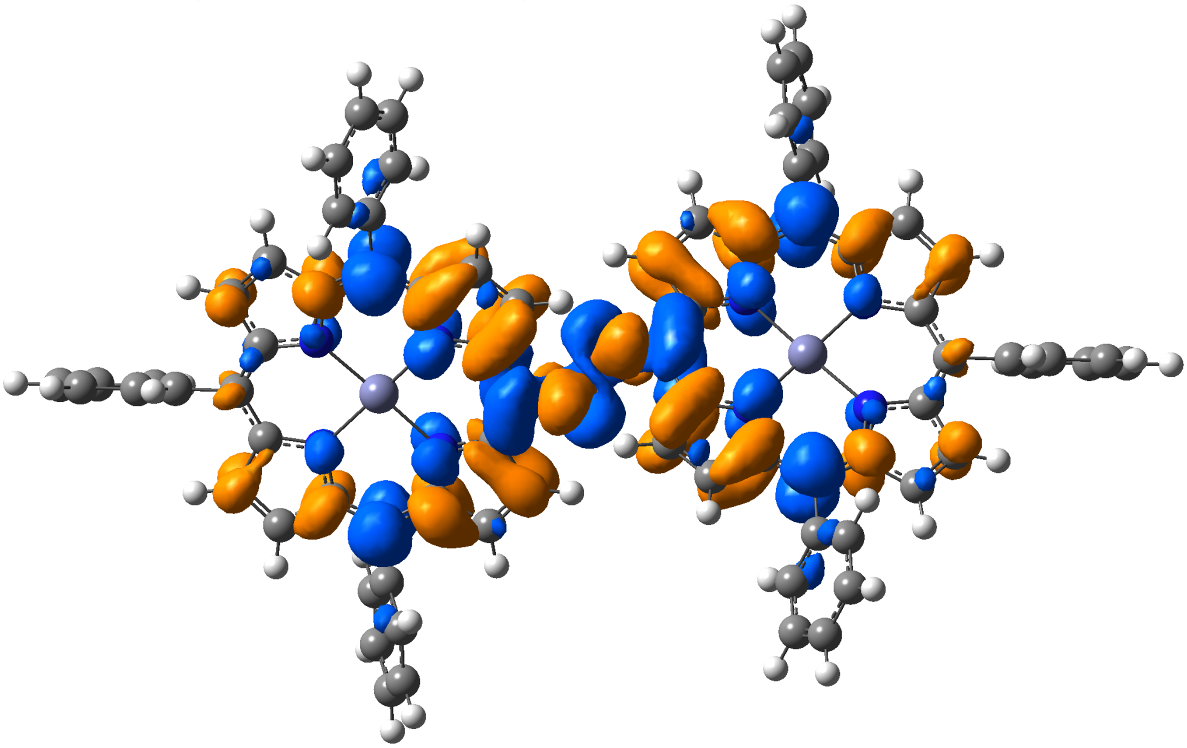


Figure S11. Observed Q band maximum plotted *vs*. the DFT-calculated HOMO-LUMO gap, according to the calibration plot of Stillman (M. J. Stillman, in *Handbook of Porphyrin Science*, eds. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010, vol. 14, pp. 461-524.) The solid line is reproduced from Figure 23 of that reference.