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Supporting Information

Electron Delocalization in Various Triply Linked Zinc(II) Porphyrin Arrays: Role of Antiaromatic Junctions between Aromatic Porphyrins

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Table S1. Energetic and structural information of triply linked porphyrin arrays.

	Point Group	Δ HOMO-LUMO (eV)	SCF Energy (hartree)	Energetic Ratio	E_{SE} (kcal mol^{-1})[a]	E_{SE} / # of units (kcal mol^{-1})	Interporphyrin Distance (Å)		HOMA		
							Neighbor	Diagonal	Porphyrin[b]	Pyrrole[c]	Junction[d]
T1	D_{4h}	3.010	-2767.3880	1.000	-	-	-	-	0.857	0.453	-
T2	D_{2h}	1.770	-5531.6142	1.999	228.8486	114.4243	8.419	-	0.908	0.590 (0.606)	0.726
T3	D_{2h}	1.325	-8295.6434	2.998	334.1091	111.3697	8.420	-	0.863 (0.763)	0.592 (0.614)	0.729
T4	D_{2h}	1.087	-11059.6730	3.996	439.5458	109.8864	8.420	-	0.905 (0.863)	0.592 (0.608)	0.734 (0.712)
T5	D_{2h}	0.937	-13823.7026	4.995	545.0444	109.0089	8.420	-	0.904 (0.884)	0.599 (0.631)	0.735 (0.728)
LS3	C_{2v}	1.400	-8295.6430	2.998	333.8657	111.2886	8.419	11.963	0.906 (0.889)	0.596 (0.610)	0.734
TS4	C_{2v}	1.251	-11059.6719	3.996	438.8560	109.7140	8.423 8.420	11.943	0.907 (0.861)	0.593 (0.617)	0.734 (0.740)
XS5	D_{4h}	1.201	-13823.6999	4.995	543.3164	108.6633	8.428	11.919	0.908 (0.838)	0.598 (0.622)	0.745
SS4	D_{4h}	1.136	-11056.1307	3.995	429.6379	107.4095	8.406	11.887	0.841	0.703 (0.601)	0.684 (0.610)[e]

[a] Stabilization energy.

[b] Average HOMA value of side (core) porphyrin unit.

[c] Average HOMA value of side (core) pyrroles.

[d] HOMA value of the naphthalene with four neighboring pyrroles.

[e] HOMA value of the octagonal core.

$$E_{SE} = (N \times E_{Z1}) - (E_{Sample} + M \times E_{hydrogen}))$$

where *N* and *M* are the numbers of the porphyrin units and removed hydrogen molecules, respectively.

Table S2. Induced ring current densities and NICS values of triply linked porphyrin arrays.

	Critical Isosurface Value				NICS / ppm			
	Porphyrin		Junction		Porphyrin		Junction	
	Terminal	Core	Naphthalene	Octagonal Core	Terminal	Core	Naphthalene	Octagonal Core
T1	0.096	-	-	-	-17.22	-	-	-
T2	0.075	-	0.097	-	-7.77	-	+21.70	-
T3	0.071	0.062	0.078	-	-8.49	-1.17	+17.38	-
T4	0.070	0.060	0.082 (0.076)[a]	-	-7.91	-1.89	+17.99 (+12.49) [a]	-
T5	0.068	0.057	0.079 (0.071) [a]	-	-7.88	-1.43 (-2.48)	+17.73 (+13.01) [a]	
LS3	0.065	0.056	0.078	-	-8.36	-2.12	+15.97	-
TS4	0.072 (0.077) [b]	0.059	0.064	-	-8.95 (-8.78) [b]	+1.97	+14.33 (+12.66) [b]	-
XS5	0.081	0.062	0.086	-	-9.23	+4.58	+12.56	-
SS4	-	0.058	0.067	0.289	-	+1.57	-2.76	65.85

[a] Outside (inside) naphthalene junction. [b] Porphyrin unit along the long (short) axis.

Figure S1. Stabilization energies of triply linked porphyrin arrays.

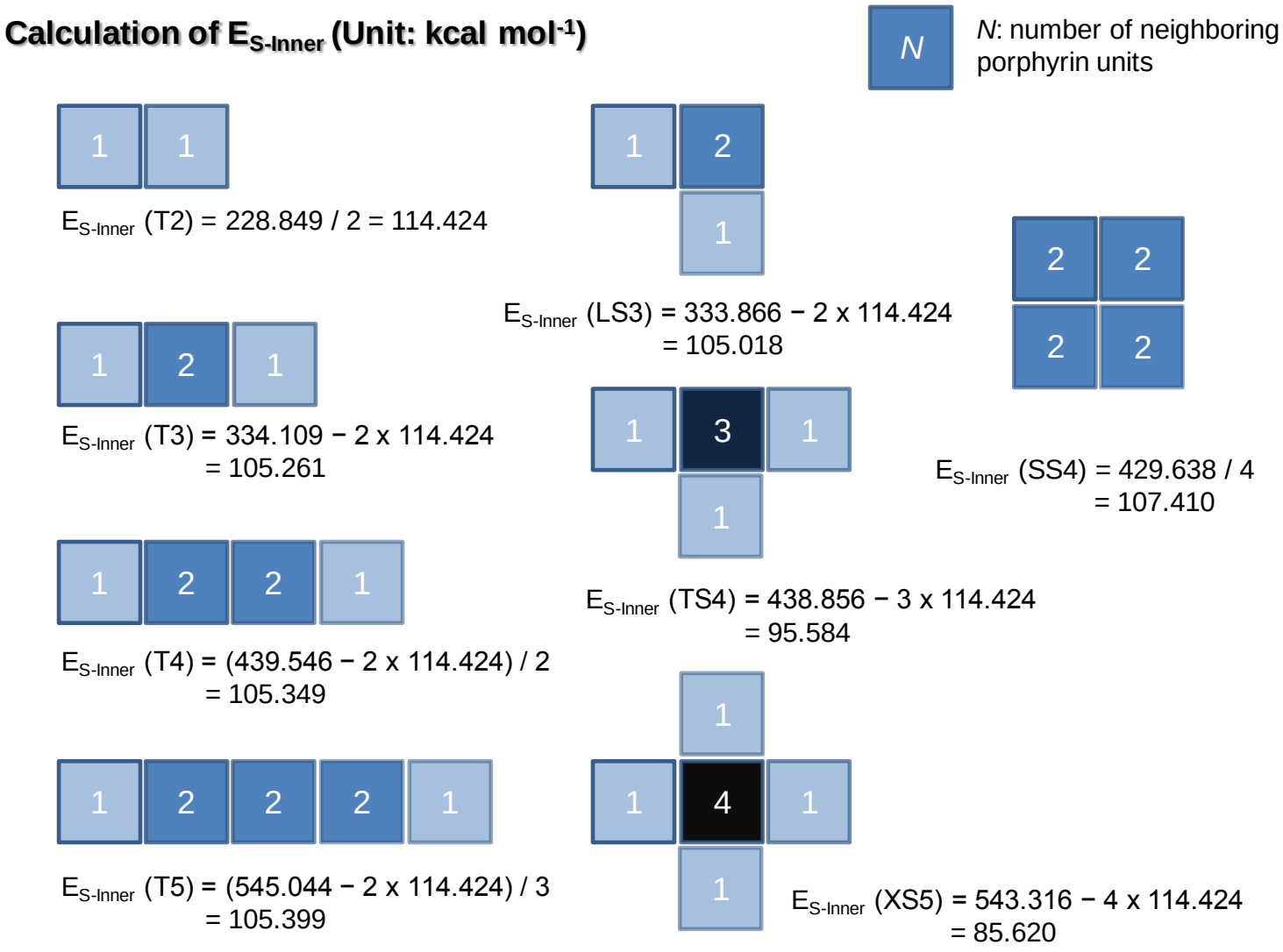
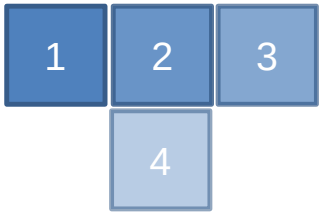


Figure S2.Averaged interporphyrin distances of **T4**,**TS4**, and **SS4**.

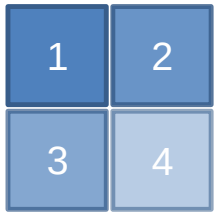
If the interporphyrin distance is *d*,

	Averaged distance	HOMO-LUMO gap (eV)
	1.667*d*	**1.087**

Por 1 (Por 4): {*d* (Por 2) + 2*d* (Por 3) + 3*d* (Por 4)} / 3 = 2*d*
Por 2 (Por 3): {*d* (Por 1) + *d* (Por 3) + 2*d* (Por 4)} / 3 = 1.333*d*

	**1.305*d* (-21.7%)**	**1.251**

Por 1 (& Por 3): {*d* (Por 2) + 2*d* (Por 3) + 1.414*d* (Por 4)} / 3 = 1.471*d*
Por 2: {*d* (Por 1) + *d* (Por 3) + *d* (Por 4)} / 3 = *d*
Por 4: {1.414*d* (Por 1) + *d* (Por 2) + 1.414 (Por 3)} / 3 = 1.276*d*

	**1.138*d* (-31.7%)**	**1.136**

Por 1 (Por 2, Por 3, & Por 4): {*d* (Por 2) + *d* (Por 3) + 1.414*d* (Por 4)} / 3 = 1.471*d*

Figure S3. ΔHOMO-LUMO values of triply linked porphyrin arrays.

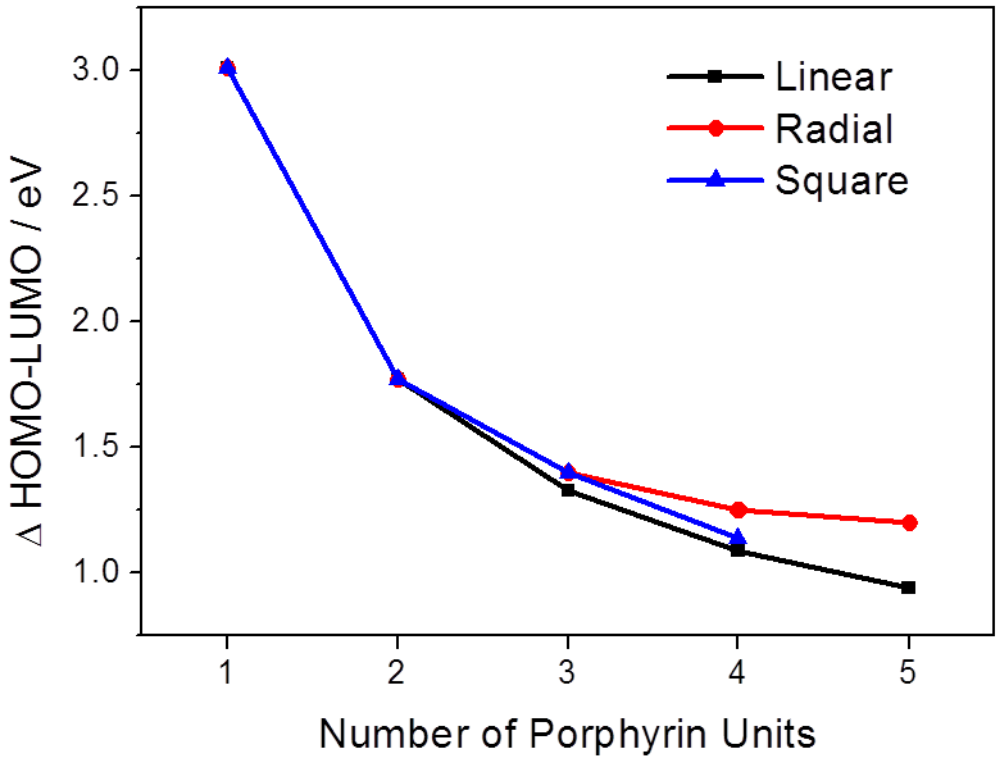


Figure S4. Induced current density maps of triply linked porphyrin arrays with critical isosurface value of 0.050.

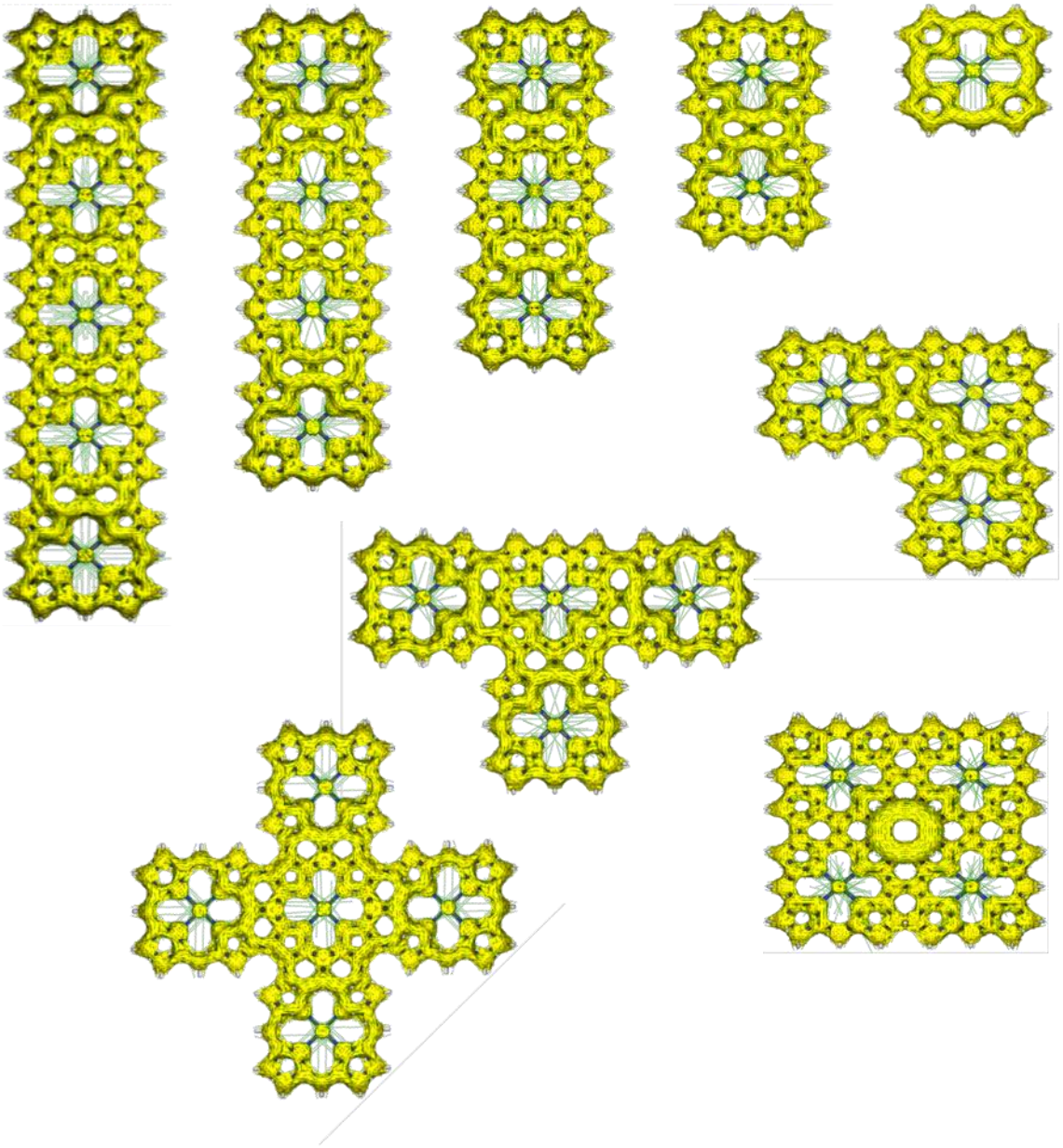
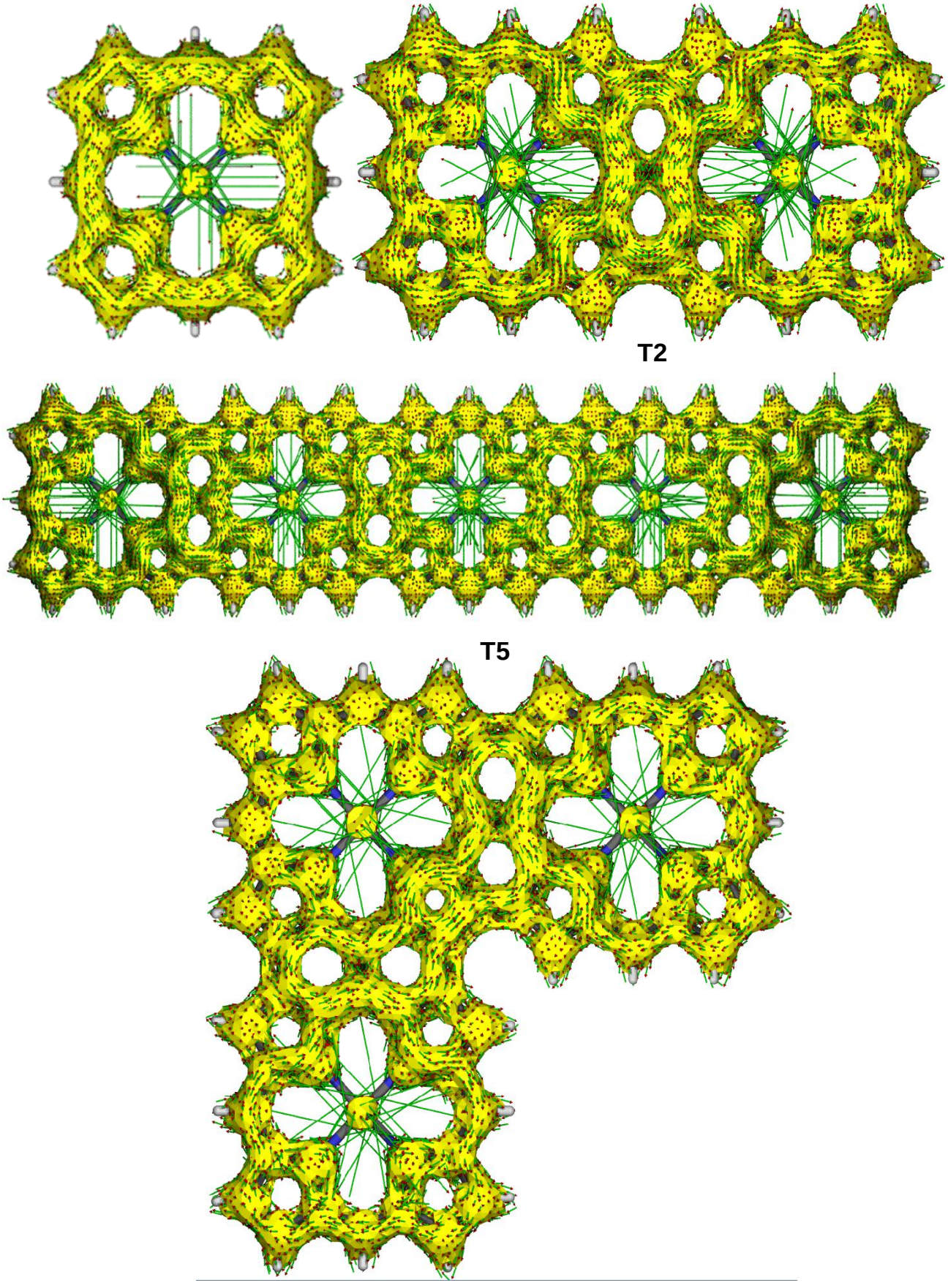
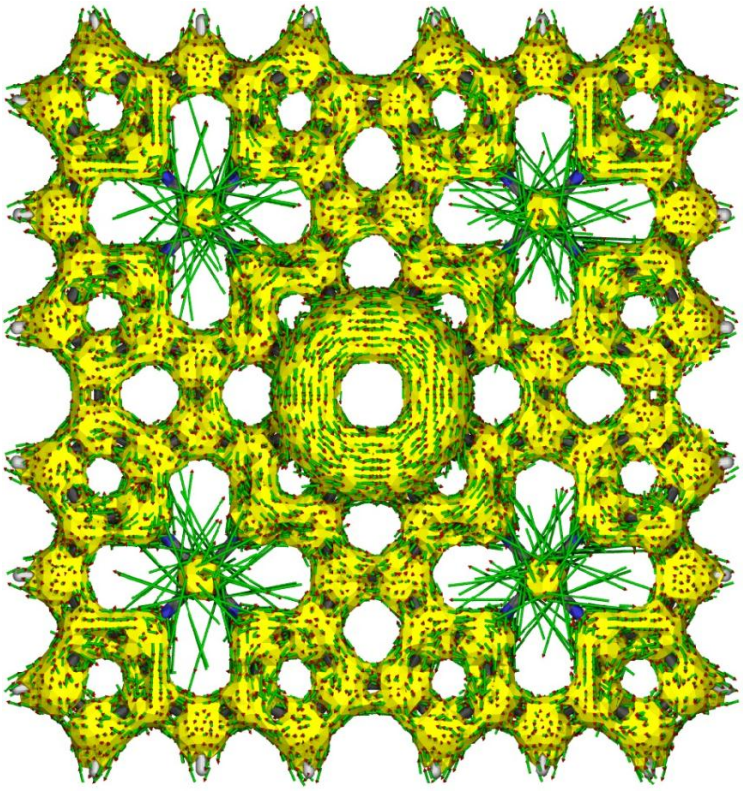


Figure S5. AICD vector maps of triply linked porphyrin arrays with critical isosurface value of 0.050



SS4



XS5

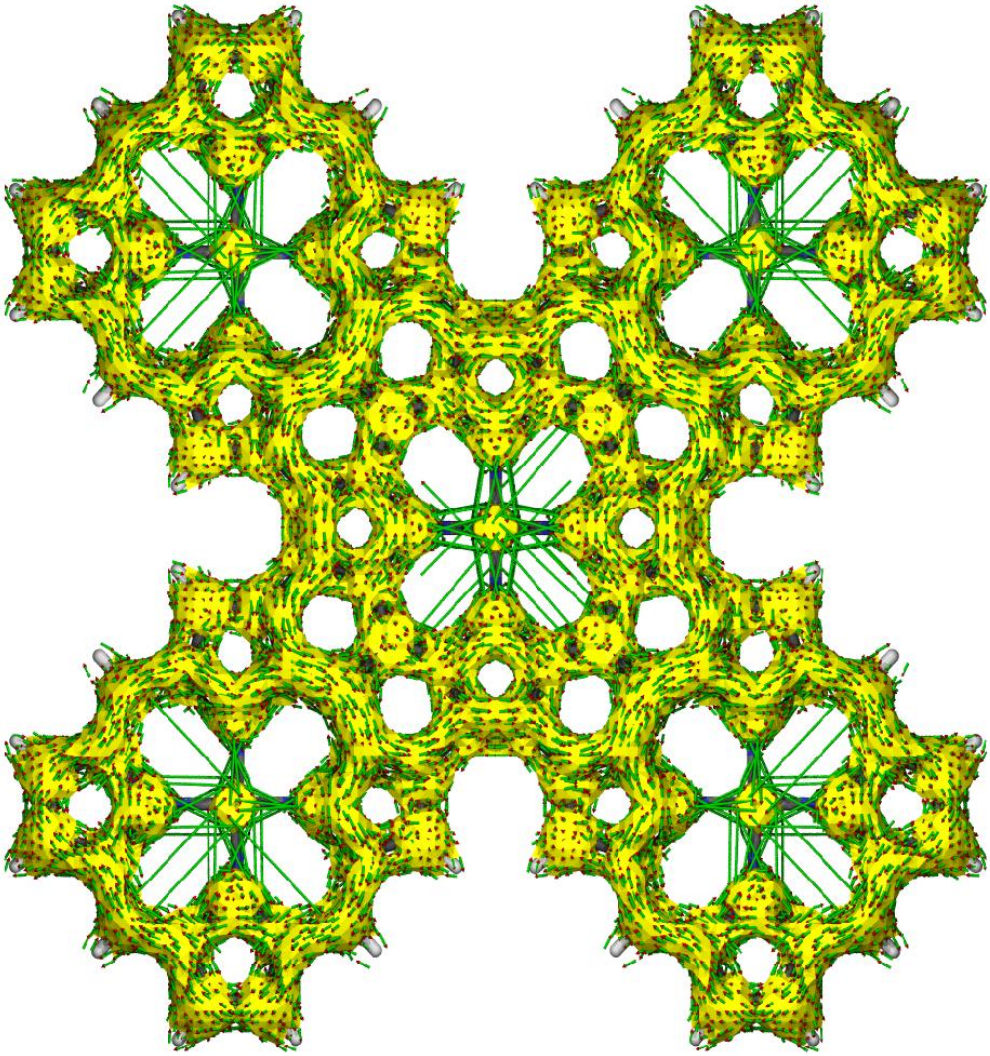


Figure S6. Frontier MOs in **T2** and its junction.

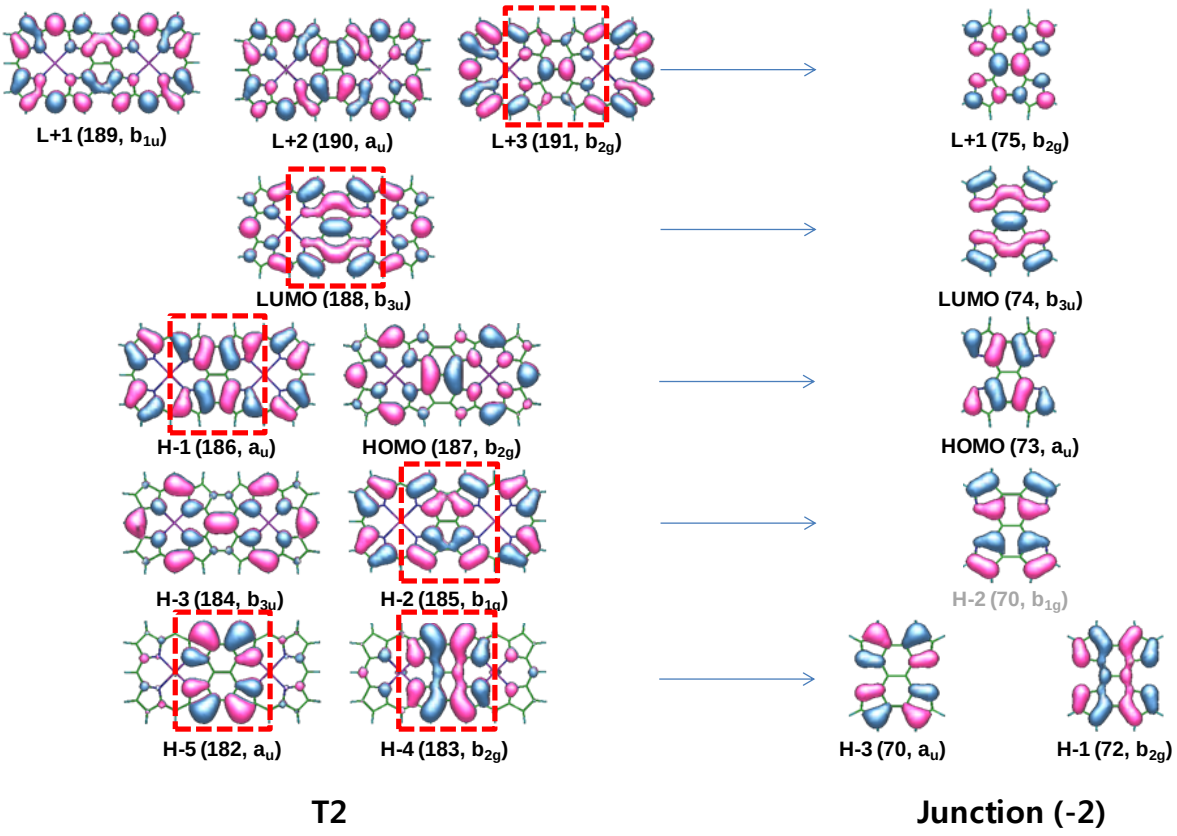
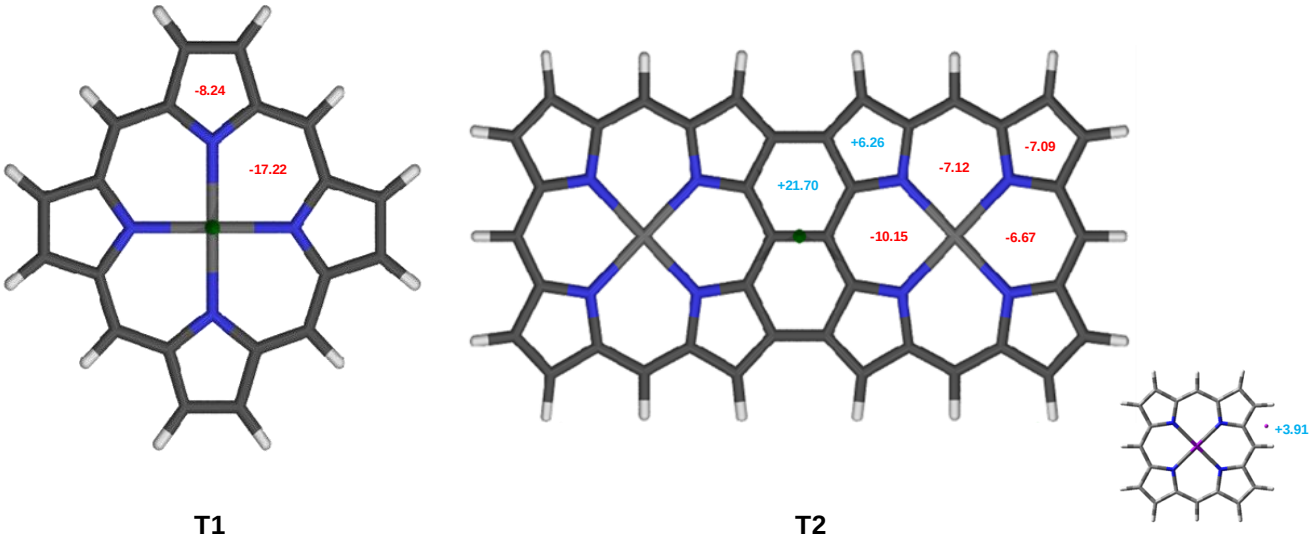
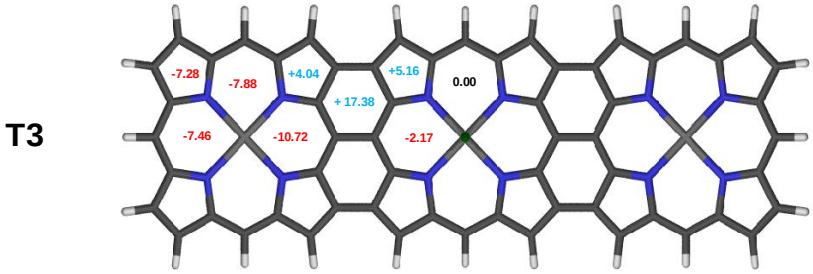
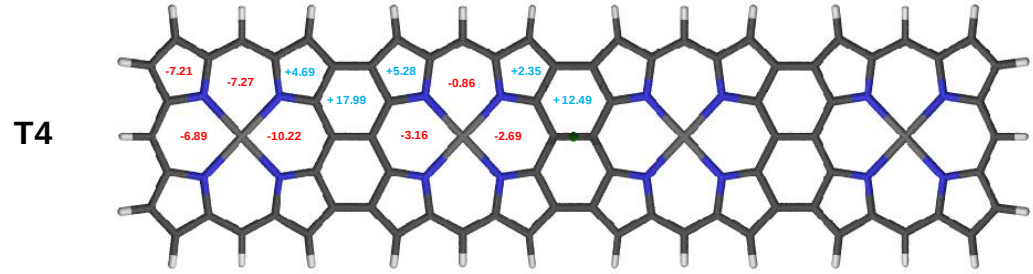
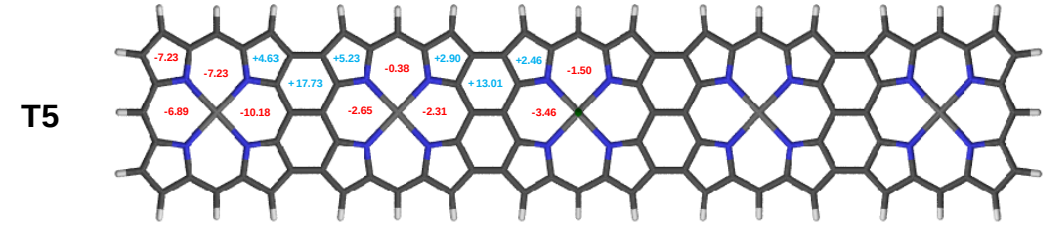


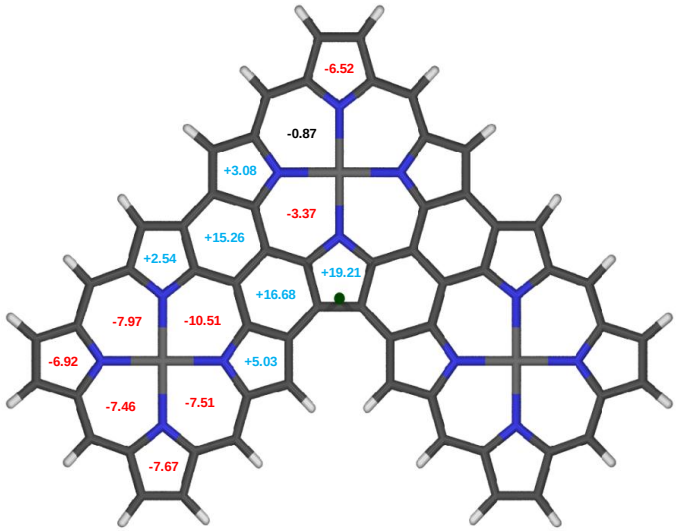
Figure S7. NICS values of monomer and triply linked porphyrin arrays.



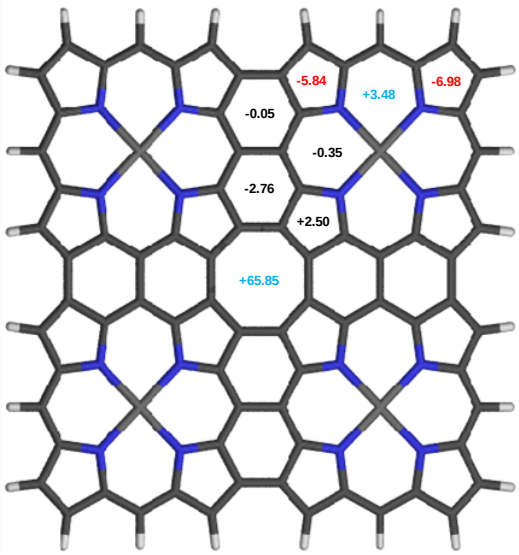




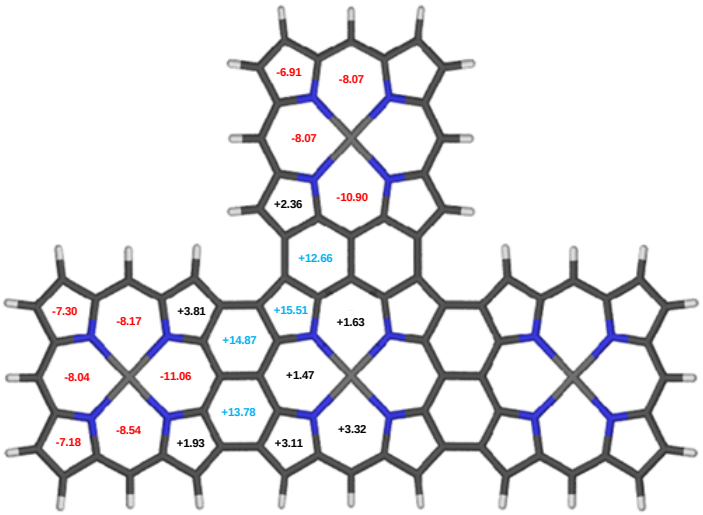




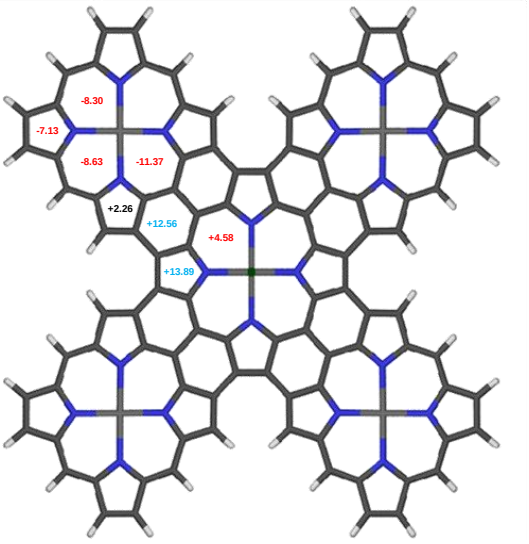
LS3



SS4

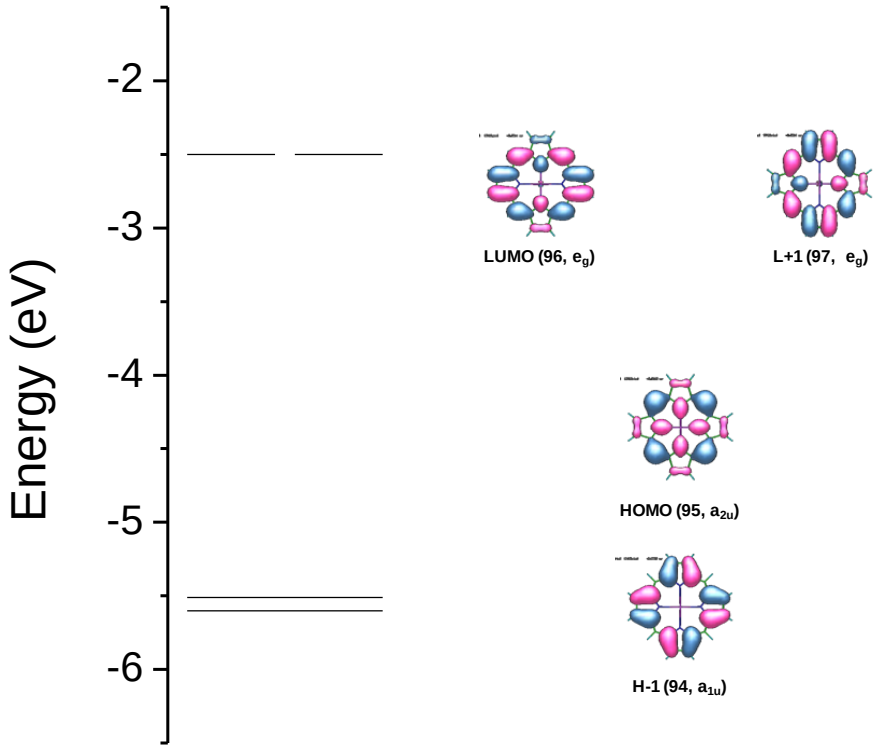


TS4

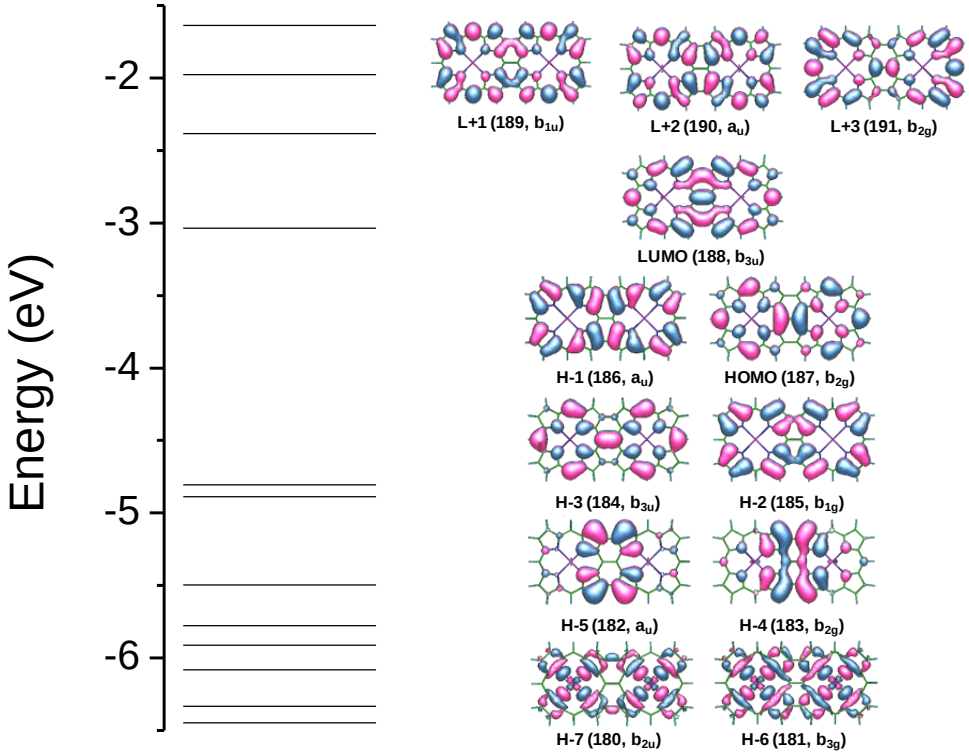


XS5

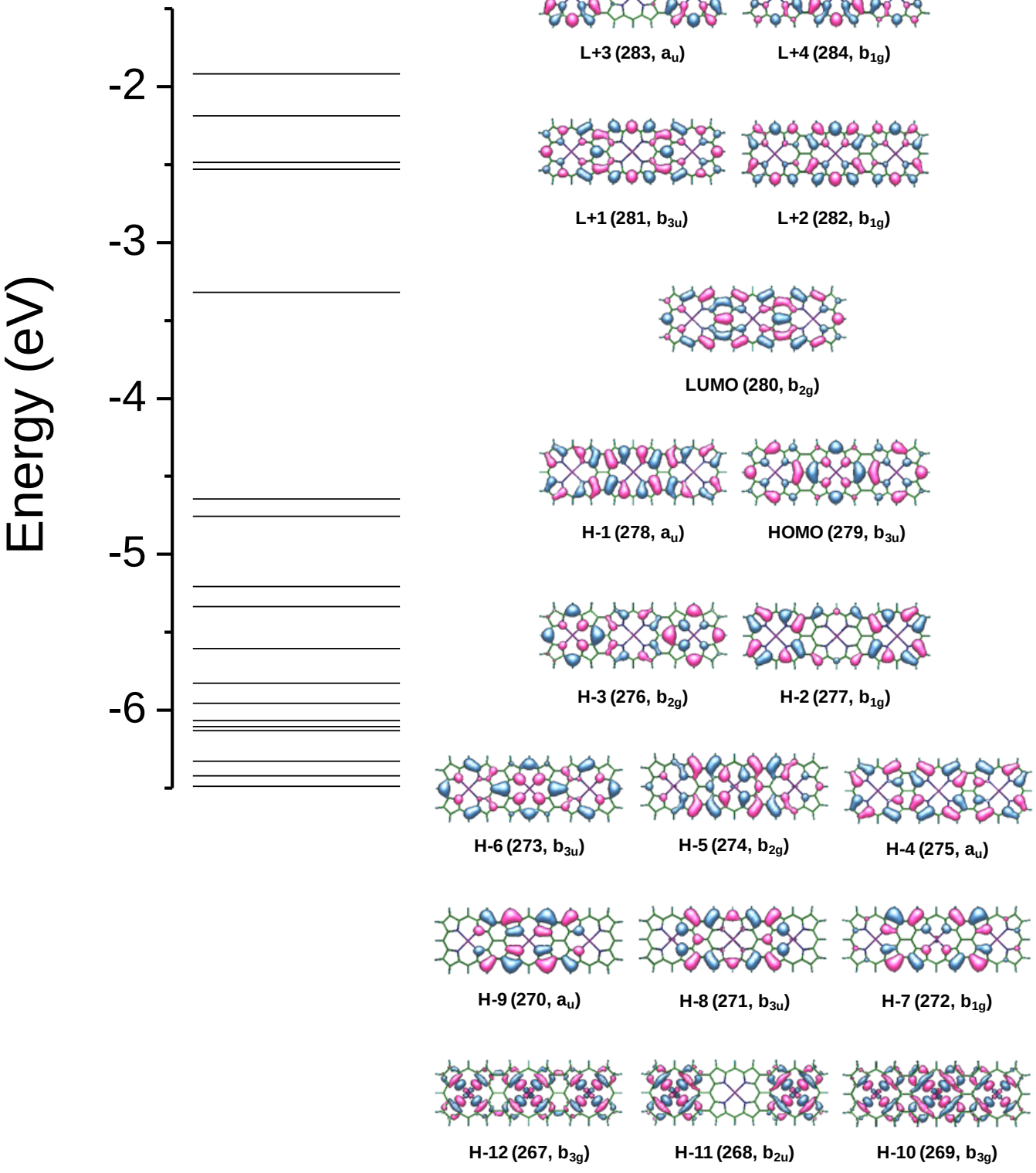
Figure S8. Frontier MOs of triply linked porphyrin arrays.



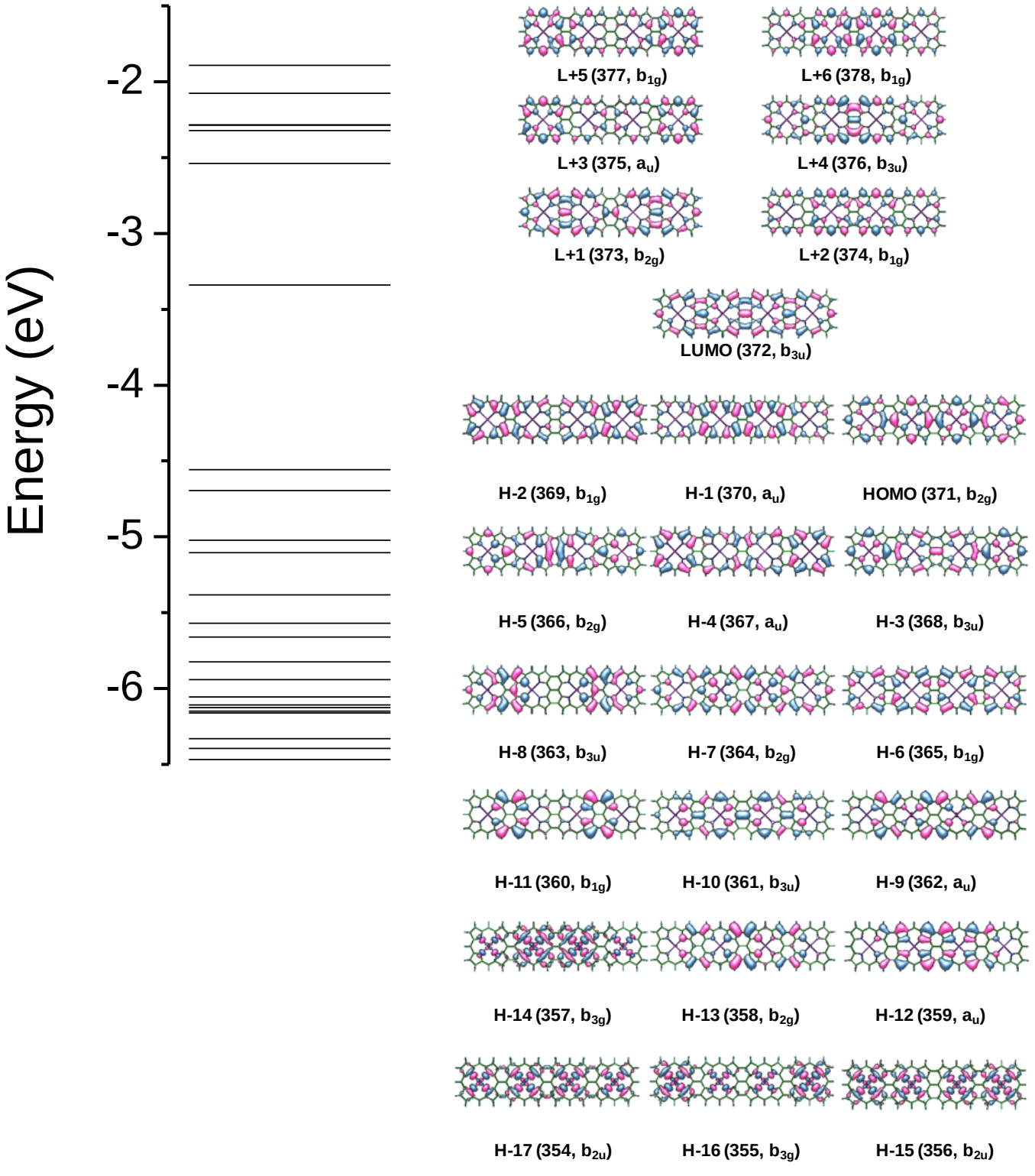
T1



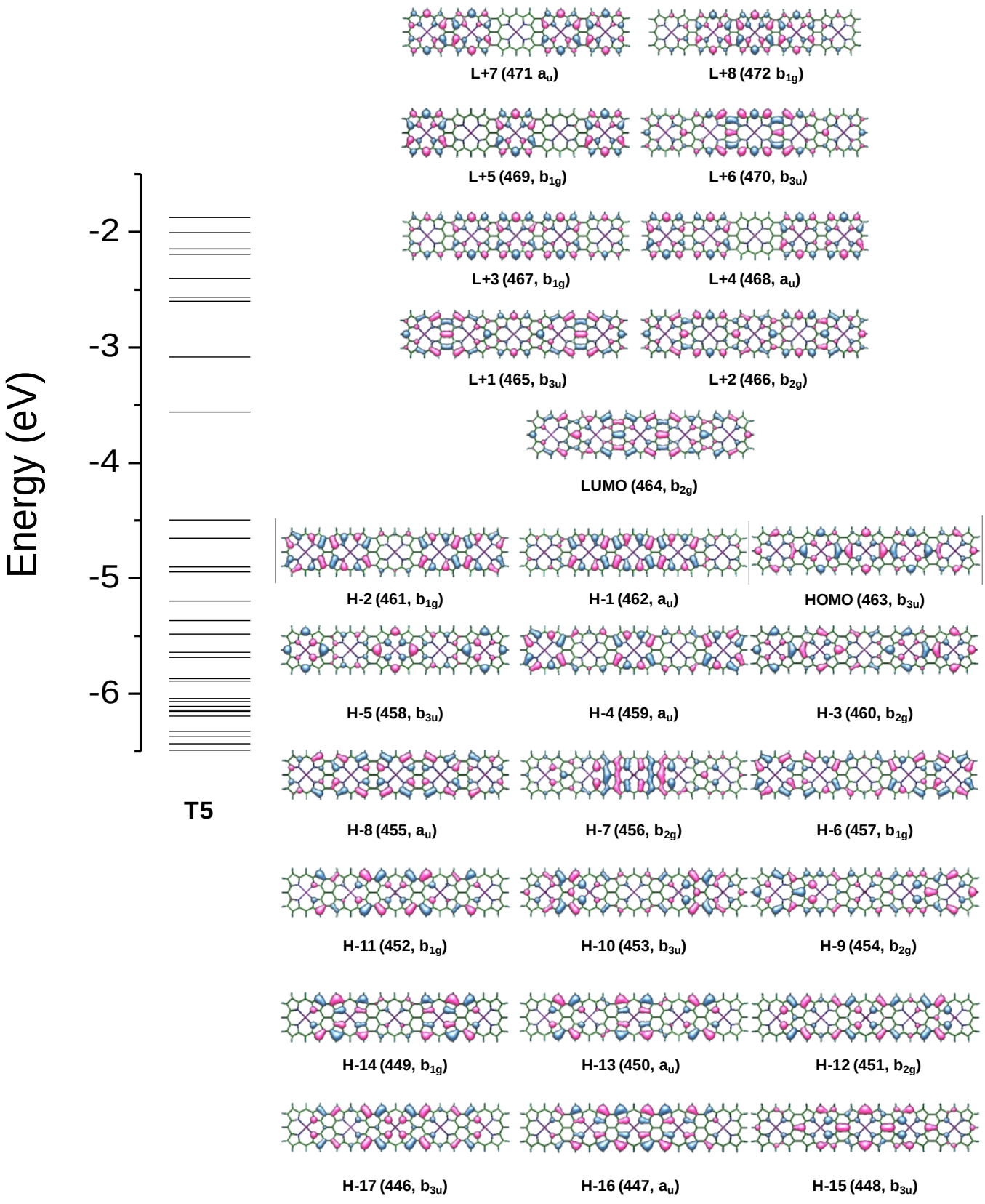
T2


Energy (eV)
-2
-3
-4
-5
-6
L+5 (285, b2g)
L+6 (286, b3u)
L+3 (283, au)
L+4 (284, b1g)
L+1 (281, b3u)
L+2 (282, b1g)
LUMO (280, b2g)
H-1 (278, au)
HOMO (279, b3u)
H-3 (276, b2g)
H-2 (277, b1g)
H-6 (273, b3u)
H-5 (274, b2g)
H-4 (275, au)
H-9 (270, au)
H-8 (271, b3u)
H-7 (272, b1g)
H-12 (267, b3g)
H-11 (268, b2u)
H-10 (269, b3g)

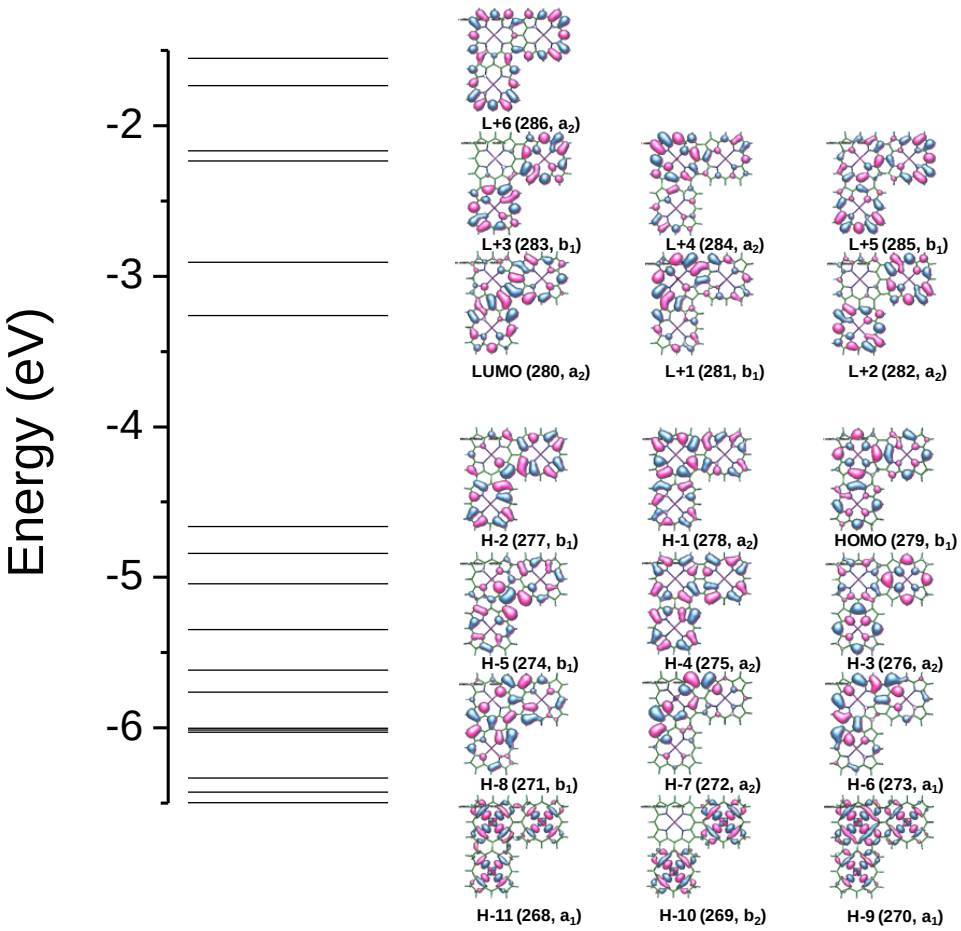
T3


Energy (eV)
-2
-3
-4
-5
-6
L+7 (379 b2g)
L+8 (380, b3u)
L+5 (377, b1g)
L+6 (378, b1g)
L+3 (375, au)
L+4 (376, b3u)
L+1 (373, b2g)
L+2 (374, b1g)
LUMO (372, b3u)
H-2 (369, b1g)
H-1 (370, au)
HOMO (371, b2g)
H-5 (366, b2g)
H-4 (367, au)
H-3 (368, b3u)
H-8 (363, b3u)
H-7 (364, b2g)
H-6 (365, b1g)
H-11 (360, b1g)
H-10 (361, b3u)
H-9 (362, au)
H-14 (357, b3g)
H-13 (358, b2g)
H-12 (359, au)
H-17 (354, b2u)
H-16 (355, b3g)
H-15 (356, b2u)

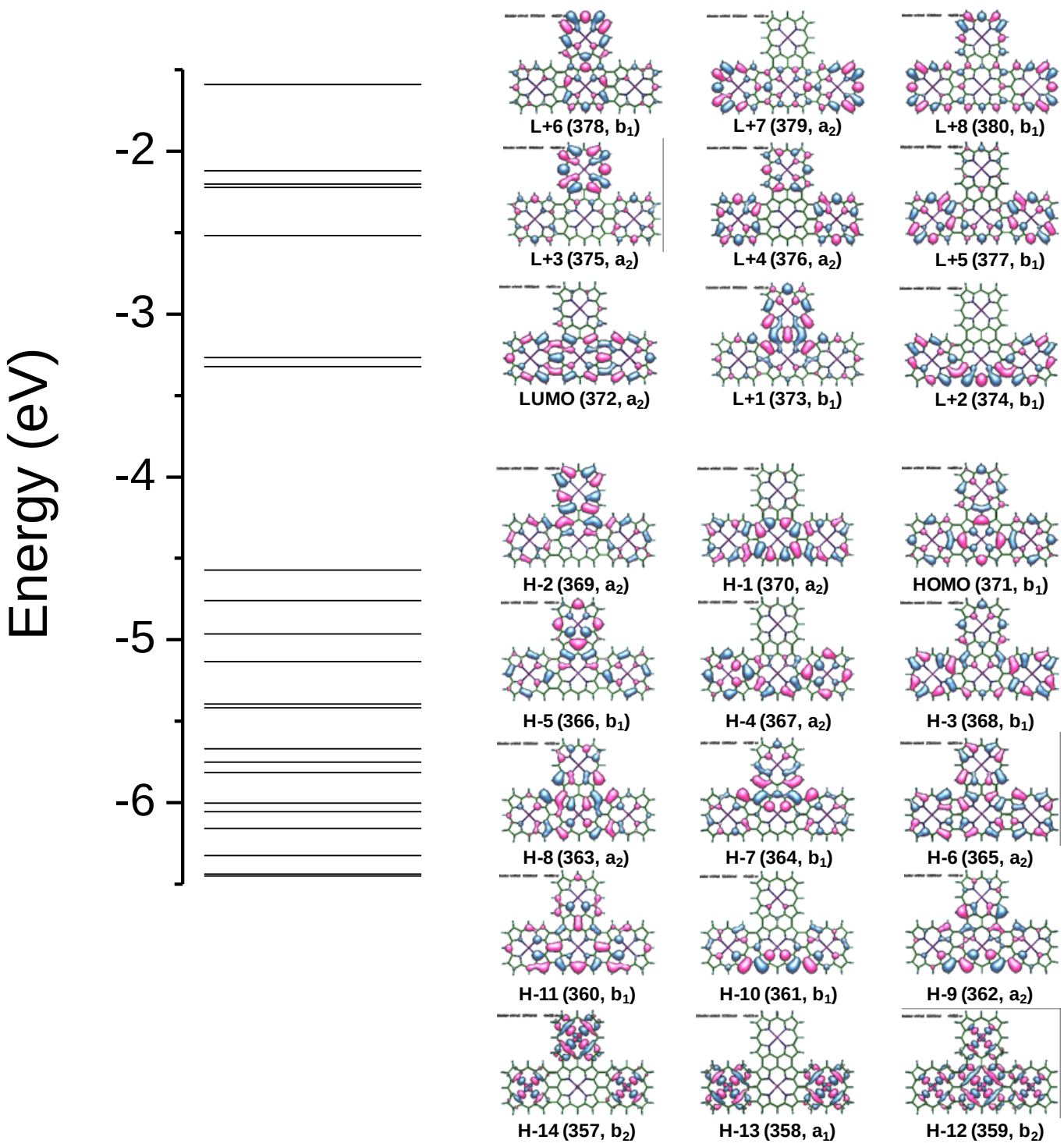
T4


Energy (eV)
-2
-3
-4
-5
-6
T5
L+7 (471 a_u)
L+8 (472 b_{1g})
L+5 (469, b_{1g})
L+6 (470, b_{3u})
L+3 (467, b_{1g})
L+4 (468, a_u)
L+1 (465, b_{3u})
L+2 (466, b_{2g})
LUMO (464, b_{2g})
H-2 (461, b_{1g})
H-1 (462, a_u)
HOMO (463, b_{3u})
H-5 (458, b_{3u})
H-4 (459, a_u)
H-3 (460, b_{2g})
H-8 (455, a_u)
H-7 (456, b_{2g})
H-6 (457, b_{1g})
H-11 (452, b_{1g})
H-10 (453, b_{3u})
H-9 (454, b_{2g})
H-14 (449, b_{1g})
H-13 (450, a_u)
H-12 (451, b_{2g})
H-17 (446, b_{3u})
H-16 (447, a_u)
H-15 (448, b_{3u})

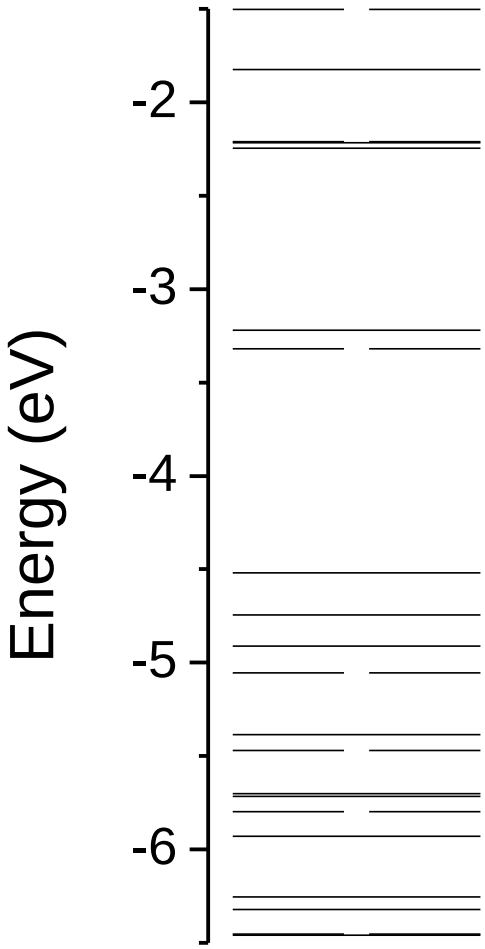
T5


Energy (eV)
-2
-3
-4
-5
-6
L+6 (286, a2)
L+3 (283, b1)
L+4 (284, a2)
L+5 (285, b1)
LUMO (280, a2)
L+1 (281, b1)
L+2 (282, a2)
H-2 (277, b1)
H-1 (278, a2)
HOMO (279, b1)
H-5 (274, b1)
H-4 (275, a2)
H-3 (276, a2)
H-8 (271, b1)
H-7 (272, a2)
H-6 (273, a1)
H-11 (268, a1)
H-10 (269, b2)
H-9 (270, a1)

LS3


Energy (eV)
-2
-3
-4
-5
-6
L+6 (378, b1)
L+7 (379, a2)
L+8 (380, b1)
L+3 (375, a2)
L+4 (376, a2)
L+5 (377, b1)
LUMO (372, a2)
L+1 (373, b1)
L+2 (374, b1)
H-2 (369, a2)
H-1 (370, a2)
HOMO (371, b1)
H-5 (366, b1)
H-4 (367, a2)
H-3 (368, b1)
H-8 (363, a2)
H-7 (364, b1)
H-6 (365, a2)
H-11 (360, b1)
H-10 (361, b1)
H-9 (362, a2)
H-14 (357, b2)
H-13 (358, a1)
H-12 (359, b2)

TS4


Energy (eV)
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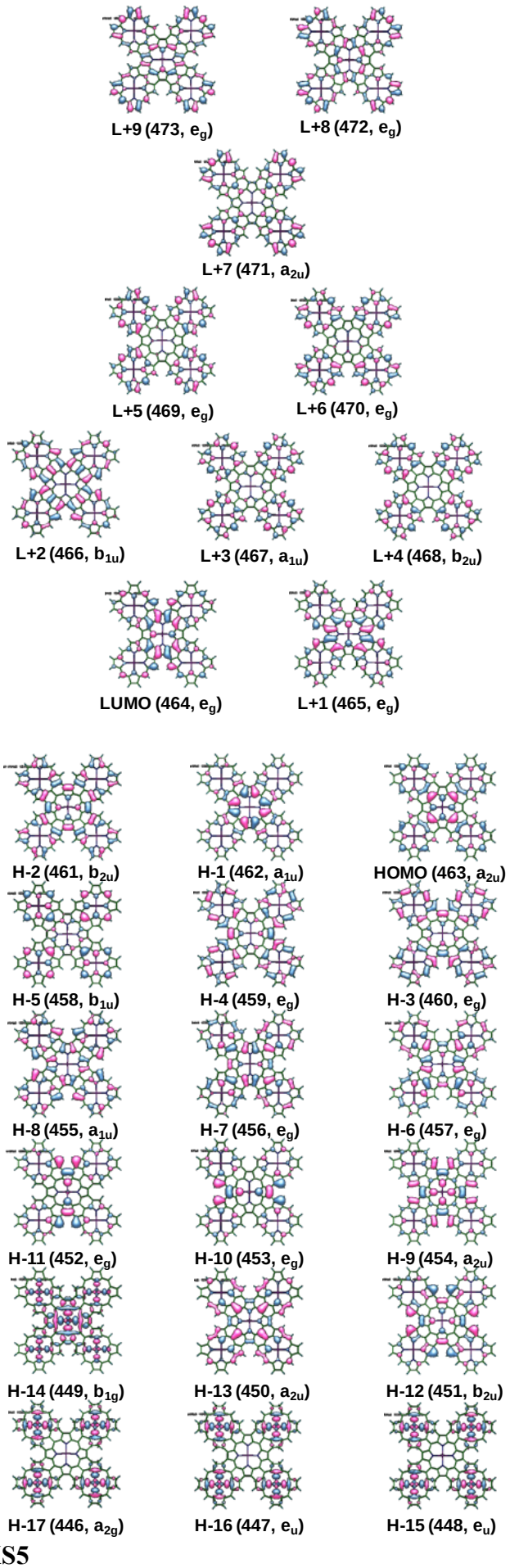
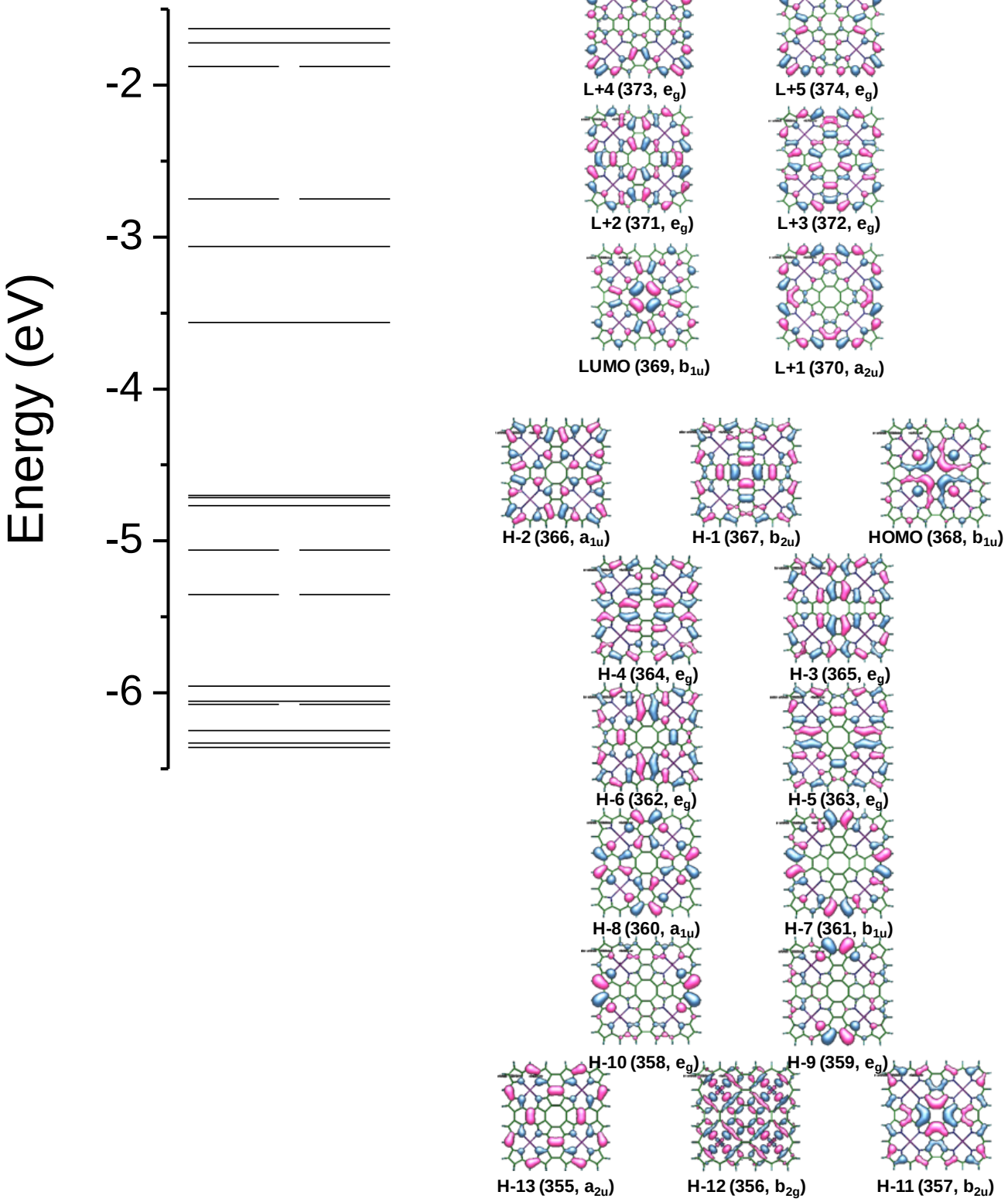
-3
-4
-5
-6

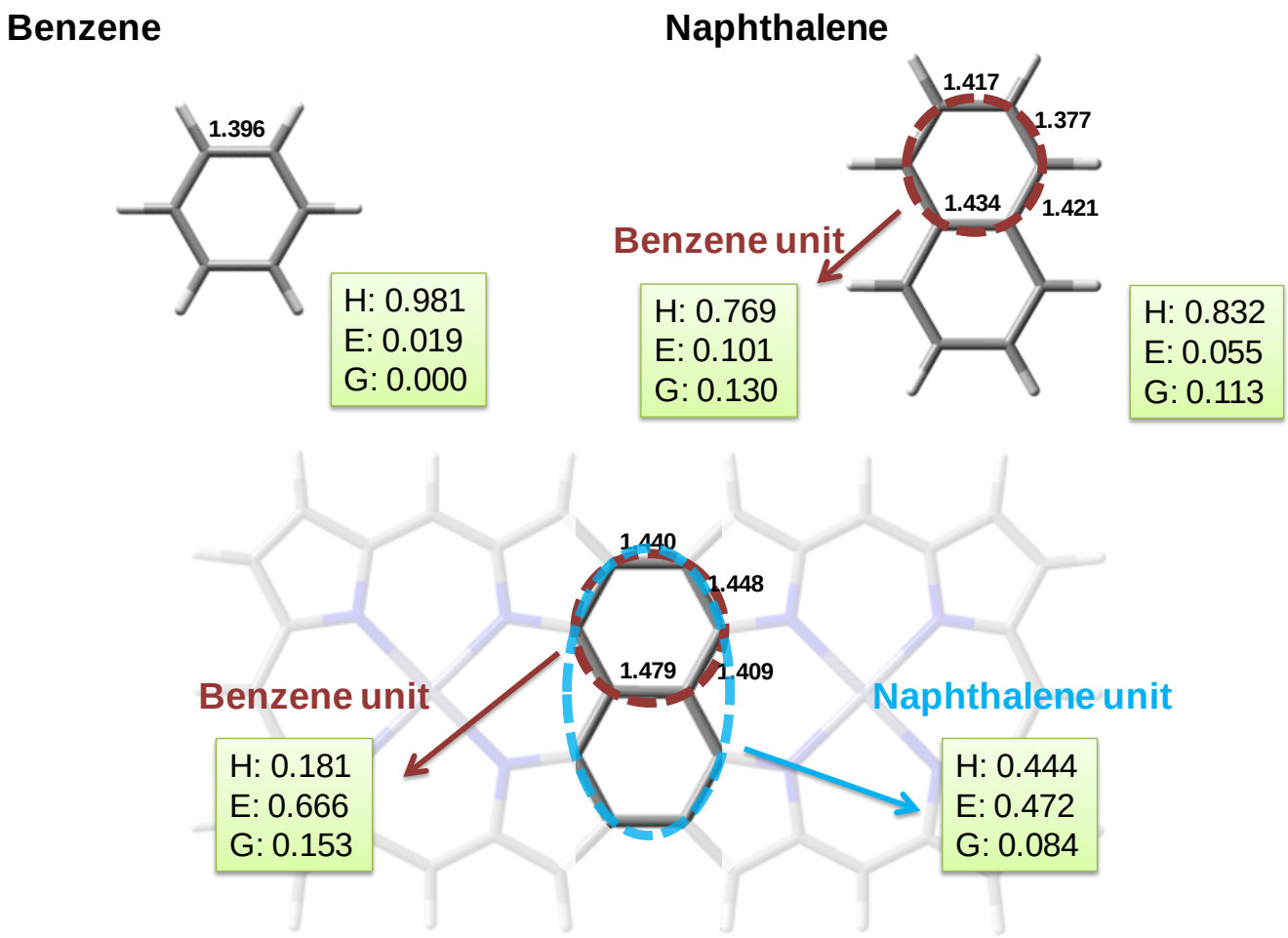

L+9 (473, e_g)
L+8 (472, e_g)
L+7 (471, a_{2u})
L+5 (469, e_g)
L+6 (470, e_g)
L+2 (466, b_{1u})
L+3 (467, a_{1u})
L+4 (468, b_{2u})
LUMO (464, e_g)
L+1 (465, e_g)
H-2 (461, b_{2u})
H-1 (462, a_{1u})
HOMO (463, a_{2u})
H-5 (458, b_{1u})
H-4 (459, e_g)
H-3 (460, e_g)
H-8 (455, a_{1u})
H-7 (456, e_g)
H-6 (457, e_g)
H-11 (452, e_g)
H-10 (453, e_g)
H-9 (454, a_{2u})
H-14 (449, b_{1g})
H-13 (450, a_{2u})
H-12 (451, b_{2u})
H-17 (446, a_{2g})
H-16 (447, e_u)
H-15 (448, e_u)

XS5


Energy (eV)
-2
-3
-4
-5
-6
L+6 (375, a1u)
L+7 (376, b2u)
L+4 (373, eg)
L+5 (374, eg)
L+2 (371, eg)
L+3 (372, eg)
LUMO (369, b1u)
L+1 (370, a2u)
H-2 (366, a1u)
H-1 (367, b2u)
HOMO (368, b1u)
H-4 (364, eg)
H-3 (365, eg)
H-6 (362, eg)
H-5 (363, eg)
H-8 (360, a1u)
H-7 (361, b1u)
H-10 (358, eg)
H-9 (359, eg)
H-13 (355, a2u)
H-12 (356, b2g)
H-11 (357, b2u)

SS4

Figure S9. HOMA values of the naphthalene unit in **T2**.



Optimized geometries by B3LYP Hamiltonian with 6-31G* basis set.

$$HOMA = 1 - \frac{\alpha}{n}\sum_i \left(R_{opt} - R_i\right)^2 = 1 - \left[\alpha\left(R_{opt} - R_{av}\right) + \frac{\alpha}{n}\sum_i \left(R_{av} - R_i\right)^2\right] = 1 - \left[EN + GEO\right]$$

where n is the number of bonds taken into the summation, α is an empirical constant chosen to give HOMA = 0 for the hypothetical Kekule structures of aromatic systems and 1 for the system with all bonds equal to the optimal value R_{opt}, and R_{av} is the average bond length.