Supporting Information

The singlet L_a and L_b bands for acenes (N = 2 to 7): A CASSCF/CASPT2 study

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Table SI1. Atom coordinates (Å) of the optimized structure (DFT/B3LYP/6-31G** level) of the studied polyacenes

Naphtalene			
Atom	X	Y	Z
C	2.43309	0.70835	0.00000
C	2.43309	-0.70835	0.00000
C	1.24465	-1.40244	0.00000
C	0.00000	-0.71670	0.00000
C	0.00000	0.71670	0.00000
C	1.24465	1.40244	0.00000
H	1.24202	-2.48942	0.00000
H	3.37725	-1.24504	0.00000
H	1.24202	2.48942	0.00000
H	3.37725	1.24504	0.00000
C	-1.24465	-1.40244	0.00000
C	-1.24465	1.40244	0.00000
C	-2.43309	0.70835	0.00000
C	-2.43309	-0.70835	0.00000
H	-3.37725	1.24504	0.00000
H	-3.37725	-1.24504	0.00000
H	-1.24202	2.48942	0.00000
H	-1.24202	-2.48942	0.00000

Antracene			
Atom	X	Y	Z
C	2.47909	1.40694	0.00000
C	1.22358	0.72246	0.00000
C	0.00000	1.40365	0.00000
C	-1.22358	0.72246	0.00000
C	-2.47909	1.40694	0.00000
C	-3.65987	0.71301	0.00000
C	-3.65987	-0.71301	0.00000
C	-2.47909	-1.40694	0.00000
C	-1.22358	-0.72246	0.00000
C	0.00000	-1.40365	0.00000
C	1.22358	-0.72246	0.00000
C	2.47909	-1.40694	0.00000
C	3.65987	-0.71301	0.00000
C	3.65987	0.71301	0.00000
H	2.47674	2.49379	0.00000
H	0.00000	2.49133	0.00000
H	-2.47674	2.49379	0.00000
H	-4.60591	1.24626	0.00000

H	-4.60591	-1.24626	0.00000
H	-2.47674	-2.49379	0.00000
H	0.00000	-2.49133	0.00000
H	2.47674	-2.49379	0.00000
H	4.60591	-1.24626	0.00000
H	4.60591	1.24626	0.00000

Tetracene			
Atom	X	Y	Z
C	4.88797	0.71526	0.00000
C	3.71056	1.40917	0.00000
C	2.45002	0.72576	0.00000
C	2.45002	-0.72576	0.00000
C	4.88797	-0.71526	0.00000
C	3.71056	-1.40917	0.00000
C	1.23516	1.40650	0.00000
C	1.23516	-1.40650	0.00000
C	0.00000	-0.72606	0.00000
C	0.00000	0.72606	0.00000
C	-1.23516	1.40650	0.00000
C	-2.45002	0.72576	0.00000
C	-2.45002	-0.72576	0.00000
C	-1.23516	-1.40650	0.00000
C	-3.71056	-1.40917	0.00000
C	-4.88797	-0.71526	0.00000
C	-3.71056	1.40917	0.00000
C	-4.88797	0.71526	0.00000
H	5.83489	1.24689	0.00000
H	3.70861	2.49600	0.00000
H	5.83489	-1.24689	0.00000
H	3.70861	-2.49600	0.00000
H	1.23519	2.49405	0.00000
H	1.23519	-2.49405	0.00000
H	-1.23519	2.49405	0.00000
H	-1.23519	-2.49405	0.00000
H	-3.70861	-2.49600	0.00000
H	-5.83489	-1.24689	0.00000
H	-5.83489	1.24689	0.00000
H	-3.70861	2.49600	0.00000

Pentacene			
Atom	X	Y	Z
C	3.67796	0.72759	0.00000
C	3.67796	-0.72759	0.00000
C	6.11676	0.71642	0.00000

C	6.11676	-0.71642	0.00000
C	4.94100	1.41037	0.00000
C	4.94100	-1.41037	0.00000
H	4.93930	2.49721	0.00000
H	7.06417	1.24724	0.00000
H	7.06417	-1.24724	0.00000
H	4.93930	-2.49721	0.00000
C	2.46720	1.40810	0.00000
C	1.22626	0.72854	0.00000
C	2.46720	-1.40810	0.00000
C	1.22626	-0.72854	0.00000
H	2.46747	-2.49564	0.00000
H	2.46747	2.49564	0.00000
C	0.00000	1.40872	0.00000
C	0.00000	-1.40872	0.00000
C	-1.22626	0.72854	0.00000
C	-1.22626	-0.72854	0.00000
H	0.00000	2.49614	0.00000
H	0.00000	-2.49614	0.00000
C	-2.46720	1.40810	0.00000
C	-2.46720	-1.40810	0.00000
C	-3.67796	0.72759	0.00000
C	-3.67796	-0.72759	0.00000
H	-2.46747	2.49564	0.00000
H	-2.46747	-2.49564	0.00000
C	-4.94100	-1.41037	0.00000
C	-4.94100	1.41037	0.00000
C	-6.11676	0.71642	0.00000
C	-6.11676	-0.71642	0.00000
H	-4.93930	2.49721	0.00000
H	-7.06417	1.24724	0.00000
H	-7.06417	-1.24724	0.00000
H	-4.93930	-2.49721	0.00000

Hexacene			
Atom	X	Y	Z
C	4.90616	0.72851	0.00000
C	4.90616	-0.72851	0.00000
C	7.34524	0.71710	0.00000
C	7.34524	-0.71710	0.00000
C	6.17061	1.41096	0.00000
C	6.17061	-1.41096	0.00000
H	6.16895	2.49780	0.00000
H	8.29295	1.24738	0.00000
H	8.29295	-1.24738	0.00000

H	6.16895	-2.49780	0.00000
C	3.69782	1.40887	0.00000
C	2.45382	0.72975	0.00000
C	3.69782	-1.40887	0.00000
C	2.45382	-0.72975	0.00000
H	3.69816	-2.49639	0.00000
H	3.69816	2.49639	0.00000
C	1.23212	1.40983	0.00000
C	1.23212	-1.40983	0.00000
C	0.00000	0.73033	0.00000
C	0.00000	-0.73033	0.00000
H	1.23234	2.49722	0.00000
H	1.23234	-2.49722	0.00000
C	-1.23212	1.40983	0.00000
C	-1.23212	-1.40983	0.00000
C	-2.45382	0.72975	0.00000
C	-2.45382	-0.72975	0.00000
H	-1.23234	2.49722	0.00000
H	-1.23234	-2.49722	0.00000
C	-3.69782	-1.40887	0.00000
C	-3.69782	1.40887	0.00000
C	-4.90616	0.72851	0.00000
C	-4.90616	-0.72851	0.00000
H	-3.69816	2.49639	0.00000
H	-3.69816	-2.49639	0.00000
C	-6.17061	1.41096	0.00000
C	-6.17061	-1.41096	0.00000
C	-7.34524	0.71710	0.00000
C	-7.34524	-0.71710	0.00000
H	-6.16895	2.49780	0.00000
H	-6.16895	-2.49780	0.00000
H	-8.29295	-1.24738	0.00000
H	-8.29295	1.24738	0.00000

Heptacene			
Atom	X	Y	Z
C	6.13547	0.72906	0.00000
C	6.13547	-0.72906	0.00000
C	8.57490	0.71739	0.00000
C	8.57490	-0.71739	0.00000
C	7.40049	1.41136	0.00000
C	7.40049	-1.41136	0.00000
H	7.39898	2.49819	0.00000
H	9.52268	1.24752	0.00000
H	9.52268	-1.24752	0.00000

H	7.39898	-2.49819	0.00000
C	4.92797	1.40945	0.00000
C	3.68248	0.73060	0.00000
C	4.92797	-1.40945	0.00000
C	3.68248	-0.73060	0.00000
H	4.92845	-2.49696	0.00000
H	4.92845	2.49696	0.00000
C	2.46294	1.41065	0.00000
C	2.46294	-1.41065	0.00000
C	1.22770	0.73156	0.00000
C	1.22770	-0.73156	0.00000
H	2.46330	2.49802	0.00000
H	2.46330	-2.49802	0.00000
C	0.00000	1.41099	0.00000
C	0.00000	-1.41099	0.00000
C	-1.22770	0.73156	0.00000
C	-1.22770	-0.73156	0.00000
H	0.00000	2.49834	0.00000
H	0.00000	-2.49834	0.00000
C	-2.46294	-1.41065	0.00000
C	-2.46294	1.41065	0.00000
C	-3.68248	0.73060	0.00000
C	-3.68248	-0.73060	0.00000
H	-2.46330	2.49802	0.00000
H	-2.46330	-2.49802	0.00000
C	-4.92797	1.40945	0.00000
C	-4.92797	-1.40945	0.00000
C	-6.13547	0.72906	0.00000
C	-6.13547	-0.72906	0.00000
H	-4.92845	2.49696	0.00000
H	-4.92845	-2.49696	0.00000
C	-7.40049	1.41136	0.00000
C	-7.40049	-1.41136	0.00000
C	-8.57490	0.71739	0.00000
C	-8.57490	-0.71739	0.00000
H	-7.39898	2.49819	0.00000
H	-9.52268	1.24752	0.00000
H	-9.52268	-1.24752	0.00000
H	-7.39898	-2.49819	0.00000

Table SI2. The number of the configuration state functions (CSF´s) of X ^1A_g generated in each one of the active space used

MCSCF Active Space	CSF´s
CAS(4,4)	8
CAS(8,8)	468
CAS(10,10)	4,936
CAS(4,4)+RAS(6,6)(S)	116
CAS(4,4)+RAS(6,6)(SD)	866
CAS(8,8)+RAS(6,6)(S)	13,252
CAS(8,8)+RAS(6,6)(SD)	105,064
CAS(14,14)	691,160

Table SI3. Squared coefficient of the dominant configurations along the polyacene series. The coefficients refer to the MCSCF wavefunction with CAS(8,8) + RAS(6,6)(S) active space

	Configuration	2	3	4	5	6	7
X ^1A_g	$HOMO^2$	80	77	80	76	75	68
	$HOMO^2 \rightarrow LUMO^2$	2	3	4	6	7	11
1 $^1B_{2u}$ (L_a)	$HOMO^1LUMO^1$	78	79	71	75	81	81
	$(HOMO-1)^1(LUMO+1)^1$	8	3	8	4	1	1
1 $^1B_{3u}$ (L_b)	$(HOMO-1)^1 LUMO^1$	36	37	41	40	42	25
	$HOMO^1(LUMO+1)^1$	34	34	32	31	32	18

$HOMO^2$ refers to the closed shell configuration. Also, in the case of naphthalene RAS(6,6) actually refers to RAS(2,2)

Table SI4. Electronic transition moment (a.u.) between 1 $^1B_{3u}$ and 1 $^1B_{2u}$ with the ground state X ^1A_g for the polyacene series using MCSCF method with several active spaces.

MCSCF	n	B_{3u}	B_{2u}
CAS (8,8)	2	-0.0598487	0.99417724
	3	-0.1063246	-1.3062771
	4	-0.187664	1.16281964
	5	-0.2675601	1.37982709
	6	-0.4264573	1.41396224
	7	-0.4442993	1.45325982
CAS (4,4)(6,6)(S)	2	0.0645967	0.89859054
	3	-0.165768	1.14282222
	4	-0.2158326	-1.3493687
	5	-0.3589058	-1.2718523
	6	-0.3814056	-1.4045118
	7	-0.4442993	1.45325982
CAS (8,8)(2,2)(S)	2	-0.0598487	0.99417724
	3	-0.165768	1.14282222
	4	-0.2158326	-1.3493687
	5	-0.3589058	-1.2718523
	6	-0.3814056	-1.4045118
	7	-0.4442993	1.45325982
CAS (8,8)(6,6)(S)	2	-0.0598487	0.99417724
	3	-0.165768	1.14282222
	4	-0.2158326	-1.3493687
	5	-0.3589058	-1.2718523
	6	-0.3814056	-1.4045118
	7	-0.4442993	1.45325982
CAS (8,8)(6,6) (SD)	2	-0.0598487	0.99417724
	3	-0.165768	1.14282222
	4	-0.2158326	-1.3493687
	5	-0.3589058	-1.2718523
	6	-0.3814056	-1.4045118
	7	-0.4442993	1.45325982
CAS (14,14)	2	-0.0844001	0.85282664
	3	-0.165768	1.14282222
	4	-0.2158326	-1.3493687
	5	-0.3589058	-1.2718523
	6	-0.3814056	-1.4045118
	7	-0.4442993	1.45325982

Table SI5. Oscillator strength (a.u.) between 1 $^1B_{3u}$ and 1 $^1B_{2u}$ with the ground state X ^1A_g for the polyacene series using CASSCF (14,14) wavefunction and energies.

MCSCF	n	B3u	B2u
CAS (8,8) (1s)	2	0.0004	0.1572
	3	0.0015	0.2124
	4	0.0042	0.1365
	5	0.0084	0.1861
	6	0.0198	0.1641
	7	0.0191	0.1583
CAS (4,4)(6,6)(S) (1s)	2	0.0000	0.1244
	3	0.0000	0.1590
	4	0.0000	0.1254
	5	0.0000	0.1502
	6	0.0000	0.1160
	7	0.0000	0.1449
CAS (8,8)(2,2)(S) (1s)	2	0.0000	0.1569
	3	0.0000	0.1587
	4	0.0000	0.1807
	5	0.0000	0.1558
	6	0.0000	0.1595
	7	0.0000	0.1832
CAS (8,8)(6,6)(S) (1s)	2	0.0004	0.1569
	3	0.0026	0.1674
	4	0.0043	0.1918
	5	0.0124	0.1490
	6	0.0145	0.1629
	7	0.0170	0.1744
CAS (8,8)(6,6) (SD) (1s)	2	0.0004	0.1581
	3	0.0025	0.1718
	4	0.0041	0.1927
	5	0.0123	0.1546
	6	0.0135	0.1590
	7	0.0164	0.1837
CAS (14,14)	2	0.0007	0.1165
	3	0.0025	0.1734
	4	0.0041	0.1941
	5	0.0121	0.1566
	6	0.0134	0.1614
	7	0.0159	0.1884

Table SI6. Oscillator strength (a.u.) between 1 $^1B_{3u}$ and 1 $^1B_{2u}$ with the ground state X ^1A_g for the polyacene series using CASSCF (14,14) wavefunction and considering excitation energies corrected by CASPT2(14,14).

CASPT2	n	B3u	B2u
CAS (8,8) (1s)	2	0.0003	0.1114
	3	0.0008	0.1518
	4	0.0021	0.0865
	5	0.0034	0.0980
	6	0.0106	0.0882
	7	0.0092	0.0792
CAS (4,4)(6,6)(S) (1s)	2	0.0000	0.0928
	3	0.0000	0.1152
	4	0.0000	0.1222
	5	0.0000	0.0935
	6	0.0000	0.0865
	7	0.0000	0.0874
CAS (8,8)(2,2)(S) (1s)	2	0.0000	0.1124
	3	0.0000	0.1130
	4	0.0000	0.1222
	5	0.0000	0.0904
	6	0.0000	0.0928
	7	0.0000	0.0864
CAS (8,8)(6,6)(S) (1s)	2	0.0004	0.1124
	3	0.0023	0.1146
	4	0.0035	0.1263
	5	0.0091	0.0908
	6	0.0093	0.0991
	7	0.0116	0.0874
CAS (8,8)(6,6) (SD) (1s)	2	0.0004	0.1121
	3	0.0023	0.1123
	4	0.0036	0.1258
	5	0.0090	0.0880
	6	0.0089	0.0918
	7	0.0106	0.0833
CAS (14,14)	2	0.0007	0.0825
	3	0.0023	0.1117
	4	0.0036	0.1245
	5	0.0086	0.0872
	6	0.0089	0.0913
	7	0.0116	0.0859

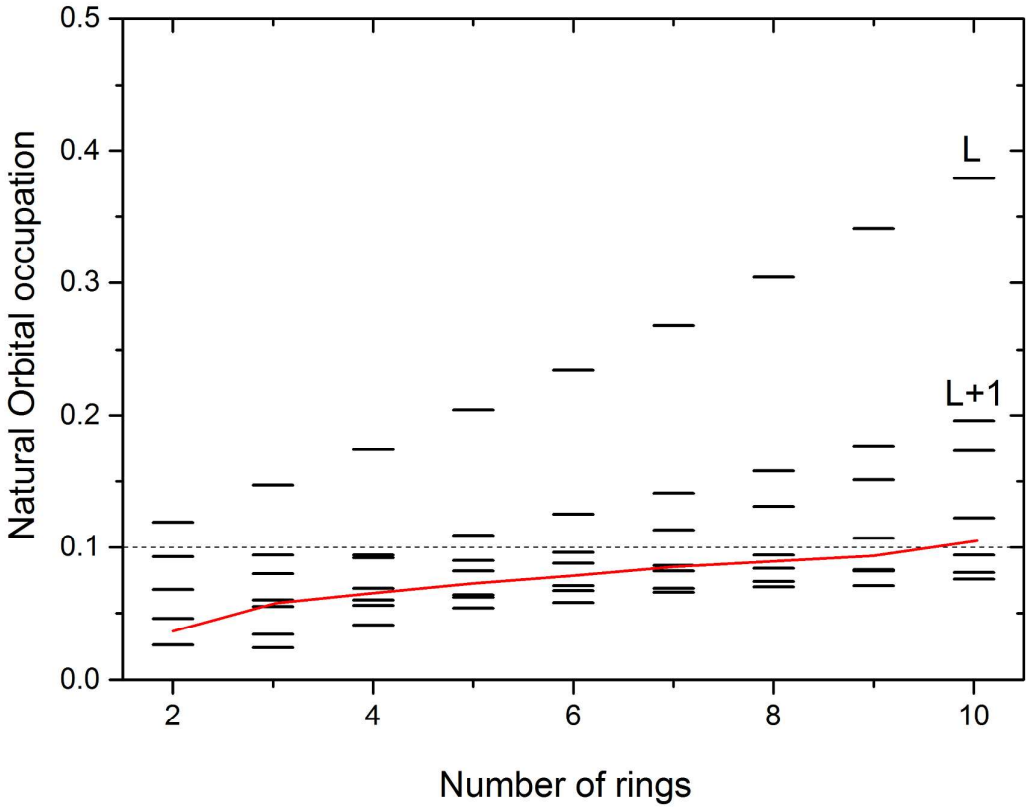

Figure SI1. AQCC natural orbital occupation of π orbitals (virtual at the RHF level) included in the active space for the acenes series in the ground state (X ^1A_g). The red line separates the orbitals included in the CAS (below the line) and RAS (above the line) active spaces. L and L+1 stand for LUMO and LUMO+1, respectively.

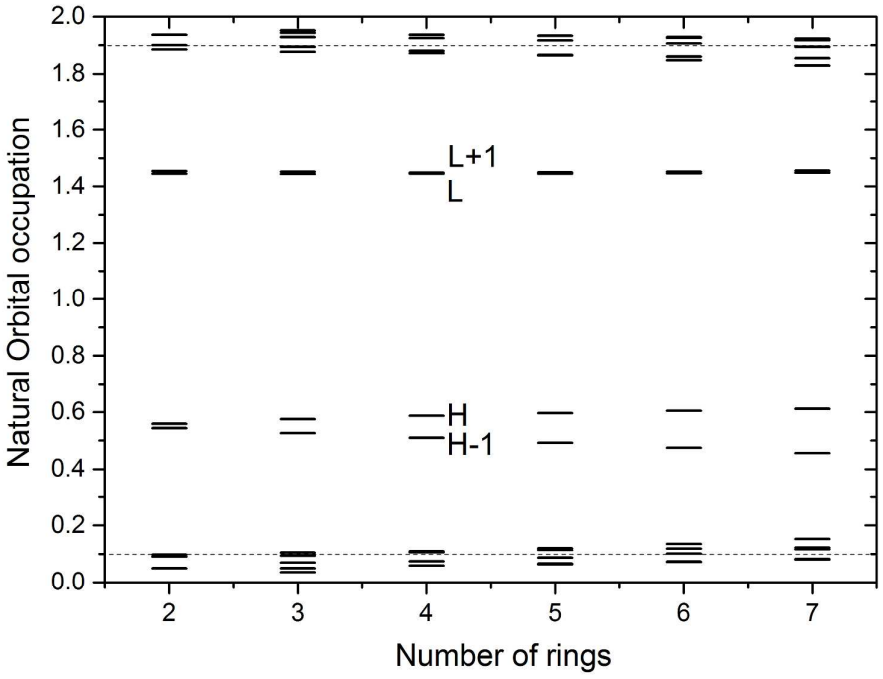

Figure SI2. AQCC natural orbital occupation of π orbitals included in the active space for the acenes series in the (1) $^1B_{3u}$ electronic state (L_b).

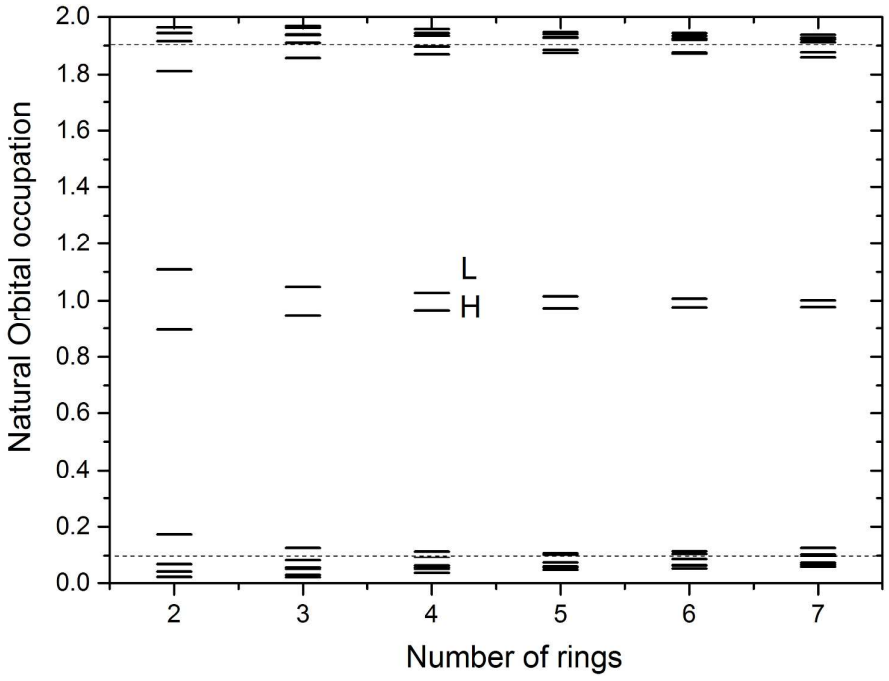

Figure SI3. AQCC natural orbital occupation of π orbitals included in the active space for the acenes series in the (1) $^1B_{2u}$ electronic state (L_a).

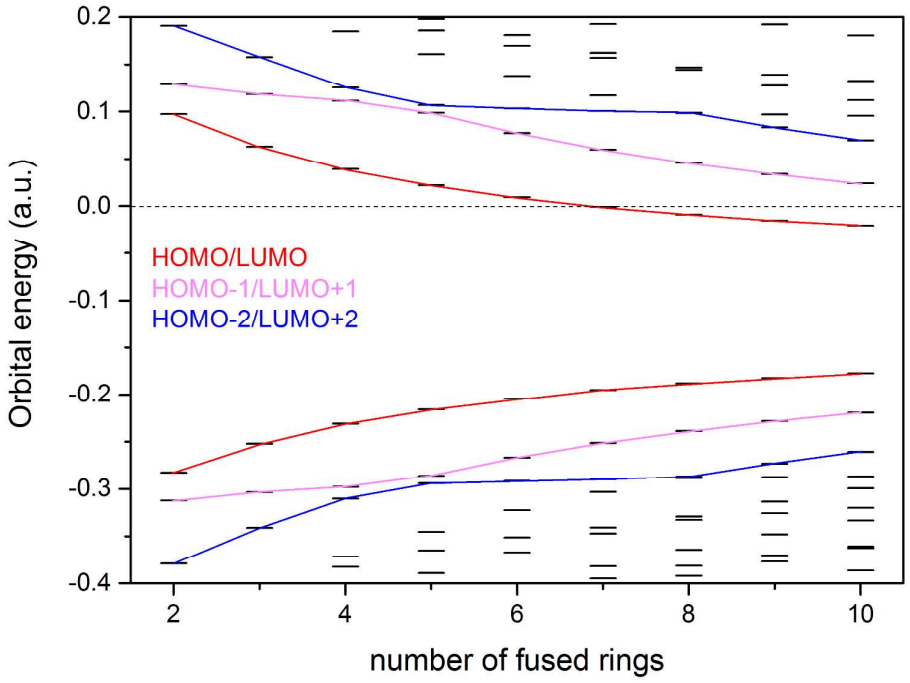

Figure SI4. RHF π orbital energies for the acenes series in the ground state (X ^1A_g). Colored lines are used to show the tendencies of the frontier orbitals.