Supplementary Information

Charge Transport Properties of Open-Shell Graphene Fragments: A Computational Study of the Phenalenyl Tilings

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Table S1. Intramolecular reorganization energies for hole (λ^+, meV) and electron (λ^-, meV) transfer of the π-radicals calculated at the B3LYP and B3LYP-D3(BJ) levels. The spin contamination for the neutral π-radical calculations, $\langle S^2 \rangle$.

Molecules	B3LYP/6-31G(d,p)			B3LYP-D3(BJ)/6-31G(d,p)		
	λ^+	λ^-	$\langle S^2 \rangle$	λ^+	λ^-	$\langle S^2 \rangle$
$C_{13}H_9$	19	35	0.801	19	34	0.801
Zigzag Odd Alternant Hydrocarbons						
$C_{19}H_{11}$	34	44	0.805	33	43	0.804
$C_{25}H_{13}$	52	58	0.813	52	58	0.812
$C_{31}H_{15}$(Z)	61	65	0.836	60	65	0.835
Armchair Odd Alternant Hydrocarbons (Phenalenyl Tilings)						
$C_{23}H_{13}$	16	27	0.811	16	26	0.811
$C_{33}H_{17}$	16	24	0.824	16	24	0.823
$C_{43}H_{21}$	16	24	0.838	16	24	0.837
Discotic Odd Alternant Hydrocarbons (Phenalenyl Tilings)						
$C_{31}H_{15}$(T)	13	20	0.808	12	20	0.808
$C_{39}H_{17}$	11	17	0.809	11	17	0.808
$C_{47}H_{19}$	10	15	0.810	9	15	0.809
$C_{55}H_{21}$	9	13	0.810	9	13	0.810
$C_{61}H_{21}$	9	13	0.805	8	11	0.805

Table S2. Intramolecular reorganization energies for hole (λ^+, meV) and electron (λ^-, meV) transfer of the π-radicals calculated at the GGA-DFT level. The spin contamination for the neutral π-radical calculations, $\langle S^2 \rangle$.

Molecules	PBE/6-31G(d,p)			BLYP/6-31G(d,p)		
	λ^+	λ^-	$\langle S^2 \rangle$	λ^+	λ^-	$\langle S^2 \rangle$
$C_{13}H_9$	15	31	0.767	15	32	0.766
Zigzag Odd Alternant Hydrocarbons						
$C_{19}H_{11}$	26	37	0.767	26	37	0.765
$C_{25}H_{13}$	39	46	0.768	39	46	0.766
$C_{31}H_{15}$(Z)	46	52	0.772	45	52	0.770
$C_{37}H_{17}$	46	52	0.778	46	53	0.781
Armchair Odd Alternant Hydrocarbons (Phenalenyl Tilings)						
$C_{23}H_{13}$	13	23	0.766	13	23	0.765
$C_{33}H_{17}$	12	20	0.766	12	20	0.765
$C_{43}H_{21}$	12	19	0.766	11	18	0.765
$C_{53}H_{25}$	12	18	0.766	12	18	0.765
Discotic Odd Alternant Hydrocarbons (Phenalenyl Tilings)						
$C_{31}H_{15}$(T)	10	18	0.764	10	18	0.763
$C_{39}H_{17}$	9	15	0.763	9	15	0.762
$C_{47}H_{19}$	8	13	0.762	8	13	0.761
$C_{55}H_{21}$	7	11	0.761	7	11	0.760
$C_{61}H_{21}$	6	10	0.760	6	10	0.759

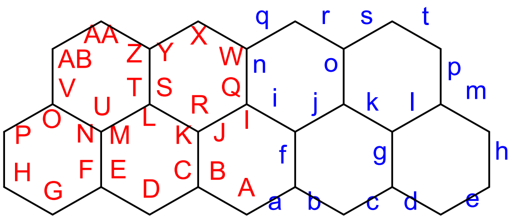
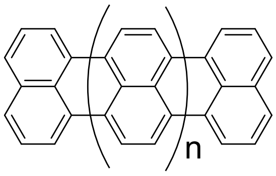


Table S3. Bond lengths (Å), bond angles (°), bond length variations (Å) and bond angle variations (°) of the $C_{31}H_{15}$(Z) calculated at the B3LYP/6-31G(d,p) level.

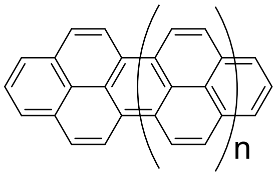
Index	Neutral	Cation	Anion	$\Delta_{C\text{-}N}$	$\Delta_{A\text{-}N}$
a	1.412	1.406	1.406	-0.006	-0.005
b	1.404	1.410	1.412	0.006	0.008
c	1.413	1.401	1.402	-0.012	-0.011
d	1.417	1.424	1.427	0.007	0.010
e	1.386	1.380	1.383	-0.006	-0.003
f	1.447	1.444	1.452	-0.004	0.005
g	1.435	1.440	1.443	0.005	0.008
h	1.400	1.407	1.404	0.007	0.004
i	1.421	1.414	1.424	-0.006	0.004
j	1.414	1.411	1.420	-0.002	0.007
k	1.425	1.419	1.424	-0.007	-0.001
l	1.426	1.426	1.429	-0.001	0.003
m	1.402	1.400	1.402	-0.002	0.000
n	1.438	1.440	1.442	0.002	0.005
o	1.441	1.443	1.444	0.002	0.003
p	1.441	1.442	1.442	0.000	0.000
q	1.413	1.414	1.411	0.001	-0.002
r	1.389	1.391	1.388	0.002	-0.001
s	1.441	1.440	1.439	0.000	-0.002
t	1.359	1.359	1.360	0.001	0.001
A	122.18	121.47	122.94	-0.72	0.76
B	118.81	119.23	118.58	0.43	-0.23
C	118.86	119.43	117.86	0.57	-1.00
D	122.03	121.45	122.70	-0.57	0.68
E	119.06	119.06	119.48	0.00	0.42
F	118.61	119.21	117.41	0.60	-1.21
G	120.81	120.36	121.37	-0.45	0.56
H	120.67	120.34	121.27	-0.33	0.60
I	120.44	120.10	120.51	-0.34	0.07
J	119.88	119.98	119.70	0.10	-0.18
K	119.94	119.76	120.24	-0.19	0.30

L	120.27	119.96	120.53	-0.32	0.26
M	119.84	120.35	119.19	0.50	-0.65
N	119.92	119.64	120.25	-0.28	0.33
O	119.21	118.71	119.88	-0.50	0.67
P	120.78	121.74	119.83	0.96	-0.95
Q	119.78	119.95	119.75	0.17	-0.03
R	120.18	120.26	120.06	0.08	-0.12
S	119.76	119.85	119.56	0.08	-0.21
T	119.96	120.19	119.92	0.23	-0.05
U	120.24	120.01	120.56	-0.23	0.32
V	118.58	118.92	118.09	0.34	-0.49
W	118.90	118.74	118.97	-0.16	0.07
X	121.90	121.90	121.96	-0.01	0.06
Y	119.48	119.31	119.71	-0.17	0.23
Z	118.27	118.26	118.15	-0.02	-0.12
AA	121.44	121.34	121.48	-0.09	0.05
AB	121.50	121.28	121.80	-0.23	0.29



Perylene-like PAHs

n = 0, Perylene
n = 1, Terrylene
n = 2, Quaterrylene
n = 3, Pentarylene



Pyrene-like PAHs

n = 0, Pyrene
n = 1, Peropyrene
n = 2, Teropyrene
n = 3, Quateropyrene
n = 4, Pentopyrene

Table S4. Intramolecular reorganization energies for hole (λ^+) and electron (λ^-) transfer of the perylene-like and pyrene-like polycyclic aromatic hydrocarbons (PAHs) calculated at the B3LYP/6-31G(d,p) level.

Molecules	λ^+	λ^-
Perylene-like PAHs		
Perylene	143	172
Terrylene	129	142
Quaterrylene	122	127
Pentarylene	121	123
Pyrene-like PAHs		
Pyrene	155	212
Peropyrene	132	176
Teropyrene	123	158
Quateropyrene	118	147
Pentopyrene	116	141

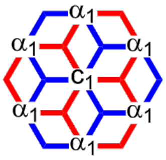
Table S5. The energy difference between the staggered and eclipsed stacking configurations (ΔE_{con}) for zigzag odd-alternant hydrocarbons calculated with different DFT functionals.

	$\Delta E_{con} = E_{eclipsed} - E_{staggered}$ (kcal/mol)		
	$C_{19}H_{11}$	$C_{25}H_{13}$	$C_{31}H_{15}$ (Z)
B3LYP-D3(BJ)	6.44	3.48	3.33
M06-2X	7.85	7.05	8.31
M06-2X-D3	7.72	6.92	8.19
M05-2X	5.28	5.19	5.95
ωB97X-D	4.99	5.81	6.98

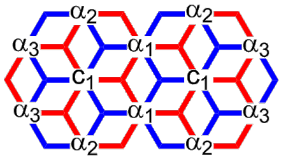
basis set: 6-31+G(d,p)//6-31G(d,p)

Table S6. Layer distance (R, in Å), spin contamination (⟨S^2⟩), singlet-triplet energy gap (ΔE_{S-T}, in eV) and binding energy (ΔE_b, in kcal/mol) of the radical π-dimers calculated with different DFT methods.

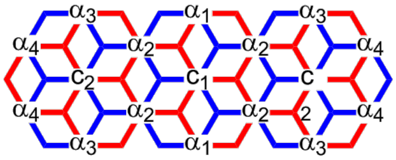
Molecules	UB3LYP-D3/6-31+G(d,p) //UB3LYP-D3/6-31G(d,p)				UM06-2X/6-31+G(d,p) //UM06-2X/6-31G(d,p)				UM06-2X-D3/6-31+G(d,p) //UM06-2X-D3/6-31G(d,p)				UM05-2X/6-31+G(d,p) //UM05-2X/6-31G(d,p)				UωB97X-D/6-31+G(d,p) //UωB97X-D/6-31G(d,p)			
	R	⟨S^2⟩	ΔE_{S-T}	ΔE_b	R	⟨S^2⟩	ΔE_{S-T}	ΔE_b	R	⟨S^2⟩	ΔE_{S-T}	ΔE_b	R	⟨S^2⟩	ΔE_{S-T}	ΔE_b	R	⟨S^2⟩	ΔE_{S-T}	ΔE_b
$C_{13}H_9$ Dimer	3.039	0.00	-0.88	-19.45	3.007	0.00	-0.91	-16.56	3.009	0.00	-0.90	-18.05	3.081	0.43	-0.64	-9.00	3.191	0.78	-0.39	-14.16
Zigzag Odd Alternant Hydrocarbons																				
$C_{19}H_{11}$ Dimer	3.122	0.00	-0.65	-24.06	3.142	0.33	-0.54	-19.58	3.146	0.31	-0.54	-22.21	3.260	0.80	-0.32	-10.39	3.289	0.98	-0.24	-20.08
$C_{25}H_{13}$ Dimer	3.217	0.53	-0.33	-27.27	3.220	0.77	-0.27	-21.89	3.224	0.77	-0.27	-25.72	3.346	1.06	-0.16	-11.83	3.341	1.18	-0.13	-26.25
$C_{31}H_{15}$(Z) Dimer	3.289	0.94	-0.14	-32.62	3.277	1.02	-0.13	-26.08	3.282	1.02	-0.13	-31.13	3.376	1.25	-0.09	-14.13	3.350	1.42	-0.09	-32.91
Phenalenyl Tilings																				
$C_{23}H_{13}$ Dimer	3.146	0.00	-0.78	-31.36	3.135	0.00	-0.77	-26.34	3.138	0.00	-0.76	-29.82	3.174	0.28	-0.61	-14.42	3.236	0.76	-0.40	-26.22
$C_{31}H_{15}$(D) Dimer	3.180	0.00	-0.78	-42.20	3.168	0.00	-0.78	-34.69	3.170	0.00	-0.77	-39.92	3.194	0.03	-0.66	-19.31	3.257	0.69	-0.41	-37.04
$C_{33}H_{17}$ Dimer	3.182	0.00	-0.77	-43.73	3.170	0.00	-0.78	-36.28	3.172	0.00	-0.78	-41.80	3.227	0.21	-0.60	-20.09	3.266	0.83	-0.40	-38.72
$C_{39}H_{17}$ Dimer	3.198	0.00	-0.79	-53.00	3.185	0.00	-0.80	-42.71	3.186	0.00	-0.80	-49.72	3.232	0.00	-0.66	-24.18	3.262	0.62	-0.45	-47.81
$C_{43}H_{21}$ Dimer	3.200	0.00	-0.76	-56.14	3.186	0.00	-0.79	-46.06	3.188	0.00	-0.79	-53.63	3.255	0.20	-0.59	-25.68	3.280	0.96	-0.40	-51.26
$C_{47}H_{19}$ Dimer	3.210	0.00	-0.80	-63.75	3.198	0.00	-0.82	-50.76	3.198	0.00	-0.82	-59.58	3.267	0.00	-0.64	-29.11	3.280	0.61	-0.44	-58.91
$C_{61}H_{21}$ Dimer	3.228	0.00	-0.81	-83.51	3.214	0.00	-0.85	-64.73	3.215	0.00	-0.85	-76.92	3.304	0.00	-0.64	-37.70	3.301	0.49	-0.47	-79.20



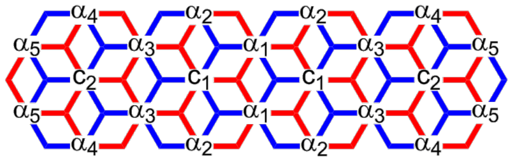
$C_{13}H_9$ Dimer



$C_{23}H_{13}$ Dimer



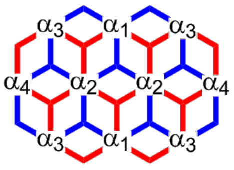
$C_{33}H_{17}$ Dimer



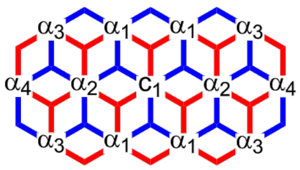
$C_{43}H_{21}$ Dimer

Table S7. Atomic distances (R, in Å) between the phenalenyl radicals and the armchair odd alternant hydrocarbons calculated with different DFT methods at the 6-31G(d,p) level.

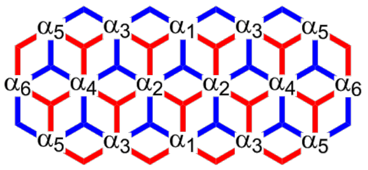
	B3LYP-D3(BJ)	M06-2X	M06-2X-D3	M05-2X	ωB97X-D
			$C_{13}H_9$ Dimer		
α_1	3.020	2.988	2.990	3.066	3.185
C_1	3.102	3.083	3.085	3.127	3.221
			$C_{23}H_{13}$ Dimer		
α_1	3.135	3.115	3.117	3.136	3.211
α_2	3.127	3.113	3.114	3.148	3.219
α_3	3.150	3.150	3.153	3.195	3.263
C_1	3.175	3.170	3.172	3.190	3.254
			$C_{33}H_{17}$ Dimer		
α_1	3.146	3.121	3.121	3.148	3.207
α_2	3.172	3.154	3.155	3.185	3.246
α_3	3.178	3.167	3.169	3.226	3.274
α_4	3.206	3.203	3.206	3.293	3.328
C_1	3.194	3.183	3.184	3.201	3.262
C_2	3.211	3.203	3.205	3.258	3.303
			$C_{43}H_{21}$ Dimer		
α_1	3.190	3.165	3.168	3.194	3.256
α_2	3.173	3.148	3.150	3.188	3.238
α_3	3.198	3.182	3.184	3.240	3.283
α_4	3.206	3.197	3.199	3.283	3.310
α_5	3.236	3.235	3.237	3.390	3.359
C_1	3.215	3.199	3.202	3.236	3.288
C_2	3.233	3.225	3.226	3.306	3.335



$C_{19}H_{11}$ Dimer



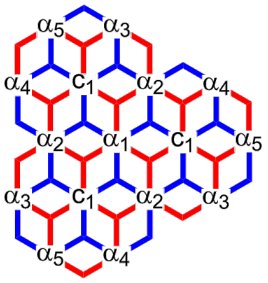
$C_{25}H_{13}$ Dimer



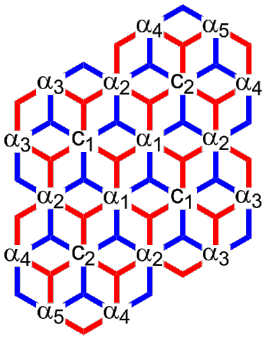
$C_{31}H_{15}$(Z) Dimer

Table S8. Atomic distances (R, in Å) between the phenalenyl radicals and the zigzag odd alternant hydrocarbons calculated with different DFT methods at the 6-31G(d,p) level.

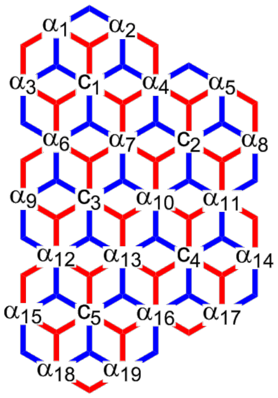
	B3LYP-D3(BJ)	M06-2X	M06-2X-D3	M05-2X	ωB97X-D
			$C_{19}H_{11}$ Dimer		
α_1	3.126	3.135	3.137	3.258	3.286
α_2	3.165	3.177	3.180	3.283	3.310
α_3	3.123	3.145	3.148	3.263	3.293
α_4	3.074	3.113	3.119	3.242	3.286
			$C_{25}H_{13}$ Dimer		
α_1	3.207	3.205	3.209	3.327	3.327
α_2	3.224	3.227	3.229	3.349	3.357
α_3	3.224	3.230	3.234	3.359	3.359
α_4	3.205	3.228	3.230	3.366	3.376
C_1	3.227	3.228	3.229	3.341	3.346
			$C_{31}H_{15}$(Z) Dimer		
α_1	3.268	3.258	3.261	3.347	3.327
α_2	3.286	3.282	3.285	3.366	3.354
α_3	3.284	3.272	3.276	3.366	3.343
α_4	3.305	3.295	3.300	3.390	3.373
α_5	3.315	3.304	3.310	3.407	3.380
α_6	3.324	3.318	3.326	3.426	3.403



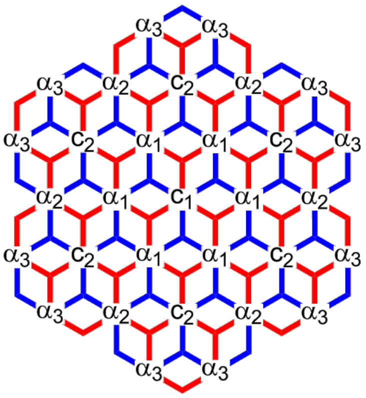
$C_{31}H_{15}$(T) Dimer



$C_{39}H_{17}$ Dimer



$C_{47}H_{19}$ Dimer



$C_{61}H_{21}$ Dimer

Table S9. Atomic distances (R, in Å) between the phenalenyl radicals and the discotic odd alternant hydrocarbons calculated with different DFT methods at the 6-31G(d,p) level.

	B3LYP-D3(BJ)	M06-2X	M06-2X-D3	M05-2X	ωB97X-D
			$C_{31}H_{15}$(D) Dimer		
α_1	3.164	3.157	3.158	3.160	3.240
α_2	3.163	3.151	3.153	3.162	3.232
α_3	3.174	3.163	3.165	3.188	3.261
α_4	3.173	3.163	3.165	3.188	3.255
α_5	3.188	3.180	3.182	3.212	3.284
C_1	3.192	3.188	3.189	3.200	3.264
			$C_{39}H_{17}$ Dimer		
α_1	3.181	3.170	3.172	3.195	3.238
α_2	3.185	3.172	3.173	3.206	3.241
α_3	3.189	3.176	3.178	3.206	3.254
α_4	3.199	3.186	3.188	3.247	3.273
α_5	3.217	3.205	3.208	3.279	3.306
C_1	3.202	3.195	3.196	3.220	3.256
C_2	3.211	3.202	3.203	3.249	3.274
			$C_{47}H_{19}$ Dimer		
α_1	3.234	3.228	3.227	3.316	3.329
α_2	3.216	3.207	3.206	3.292	3.300
α_3	3.216	3.205	3.206	3.283	3.297
α_4	3.198	3.187	3.187	3.252	3.270
α_5	3.209	3.200	3.201	3.268	3.291
α_6	3.193	3.181	3.182	3.233	3.257
α_7	3.192	3.186	3.186	3.241	3.270

α_8	3.208	3.195	3.197	3.258	3.283
α_9	3.178	3.164	3.166	3.198	3.225
α_{10}	3.188	3.180	3.179	3.231	3.261
α_{11}	3.198	3.185	3.185	3.239	3.262
α_{12}	3.193	3.181	3.182	3.233	3.257
α_{13}	3.192	3.186	3.186	3.241	3.270
α_{14}	3.208	3.195	3.197	3.258	3.283
α_{15}	3.216	3.205	3.206	3.283	3.297
α_{16}	3.198	3.187	3.187	3.252	3.270
α_{17}	3.209	3.200	3.201	3.268	3.291
α_{18}	3.234	3.228	3.227	3.316	3.329
α_{19}	3.216	3.207	3.206	3.292	3.300
C_1	3.221	3.212	3.213	3.283	3.299
C_2	3.212	3.204	3.205	3.263	3.284
C_3	3.204	3.199	3.200	3.248	3.272
C_4	3.212	3.204	3.205	3.263	3.284
C_5	3.221	3.212	3.213	3.283	3.299
			$C_{61}H_{21}$ Dimer		
α_1	3.202	3.194	3.195	3.275	3.285
α_2	3.216	3.201	3.201	3.283	3.279
α_3	3.237	3.221	3.223	3.313	3.310
C_1	3.203	3.205	3.206	3.283	3.292
C_2	3.226	3.215	3.216	3.299	3.298

Table S10. The gas-phase disproportionation enthalpies (ΔH_{disp}, in eV) of the π-radicals calculated at the B3LYP/6-31+G(d)//B3LYP/6-31G(d,p) level. The disproportionation potential of the π-radicals (ΔE_{sum}, in V) obtained from the experimental results. The electronic coupling (*t*, in eV) of the radical π-dimers calculated with the PW91PW91/DZP method at the B3LYP-D3(BJ)/6-31G(d,p) optimized structures.

	ΔH_{disp}	Decreasing ratio of ΔH_{disp}	ΔE_{sum}	Decreasing ratio of ΔE_{sum}	t	Decreasing ratio of t	Ratio of $4\|t\|/\Delta H_{disp}$	Ratio of $4\|t\|/\Delta E_{sum}$
$C_{13}H_9$	5.02	1.00	1.60	1.00	0.680	1.00	1.00	1.00
Zigzag Odd Alternant Hydrocarbons								
$C_{19}H_{11}$	4.44	0.88	—	—	0.546	0.80	0.91	—
$C_{25}H_{13}$	4.13	0.82	—	—	0.382	0.56	0.68	—
$C_{31}H_{15}$(Z)	3.91	0.78	—	—	0.250	0.37	0.47	—
Phenalenyl Tilings								
$C_{23}H_{13}$	4.00	0.80	1.10	0.69	0.553	0.81	1.02	1.18
$C_{31}H_{15}$(D)	3.57	0.71	0.70	0.44	0.517	0.76	1.07	1.74
$C_{33}H_{17}$	3.40	0.68	—	—	0.508	0.75	1.10	—
$C_{39}H_{17}$	3.26	0.65	—	—	0.499	0.73	1.13	—
$C_{43}H_{21}$	3.00	0.60	—	—	0.479	0.70	1.18	—
$C_{47}H_{19}$	2.99	0.60	—	—	0.485	0.71	1.20	—
$C_{61}H_{21}$	2.71	0.54	—	—	0.470	0.69	1.28	—

Note: All the ratio values of the extended π-radicals were compared with the phenalenyl radical.

Table S11. Site energies (ε_1 and ε_2, in eV), charge transfer integral (J_{12}, in eV), spatial overlap (S_{12}) and electronic coupling (t, in eV) of the radical π-dimers calculated with the PW91PW91/DZP method at the B3LYP-D3(BJ)/6-31G(d,p) optimized structures.

	ε_1	ε_2	J_{12}	S_{12}	t
$C_{13}H_9$	-4.319	-4.319	1.172	-0.116	0.680
$C_{19}H_{11}$	-4.387	-4.387	0.958	-0.095	0.546
$C_{25}H_{13}$	-4.449	-4.449	-0.688	0.069	-0.382
$C_{31}H_{15}$(Z)	-4.503	-4.503	0.460	-0.047	0.250
$C_{23}H_{13}$	-4.398	-4.398	-0.975	0.097	-0.553
$C_{31}H_{15}$(D)	-4.457	-4.457	0.917	-0.091	0.517
$C_{33}H_{17}$	-4.456	-4.456	-0.904	0.090	-0.508
$C_{39}H_{17}$	-4.506	-4.506	-0.889	0.087	-0.499
$C_{43}H_{21}$	-4.498	-4.498	-0.858	0.085	-0.479
$C_{47}H_{19}$	-4.546	-4.546	-0.867	0.085	-0.485
$C_{61}H_{21}$	-4.616	-4.616	-0.843	0.081	-0.470

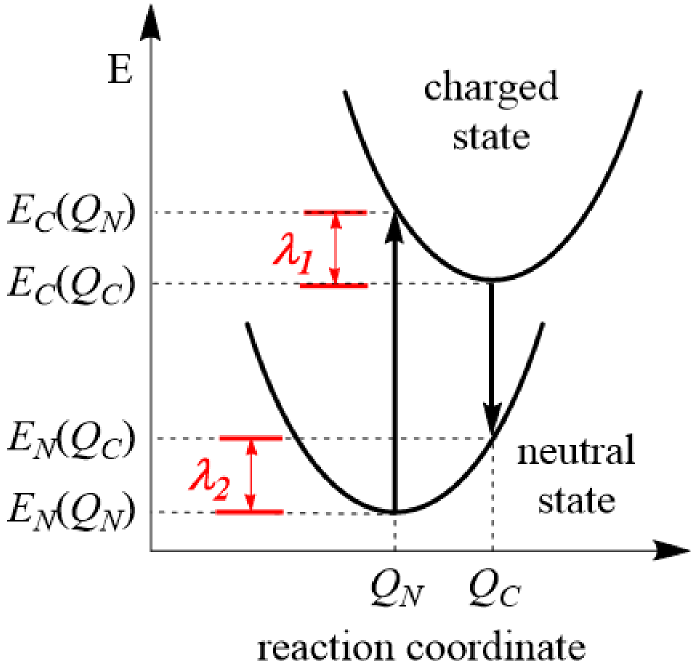


Fig. S1 Schematic illustration of intramolecular reorganization energy calculated by the four-point method.

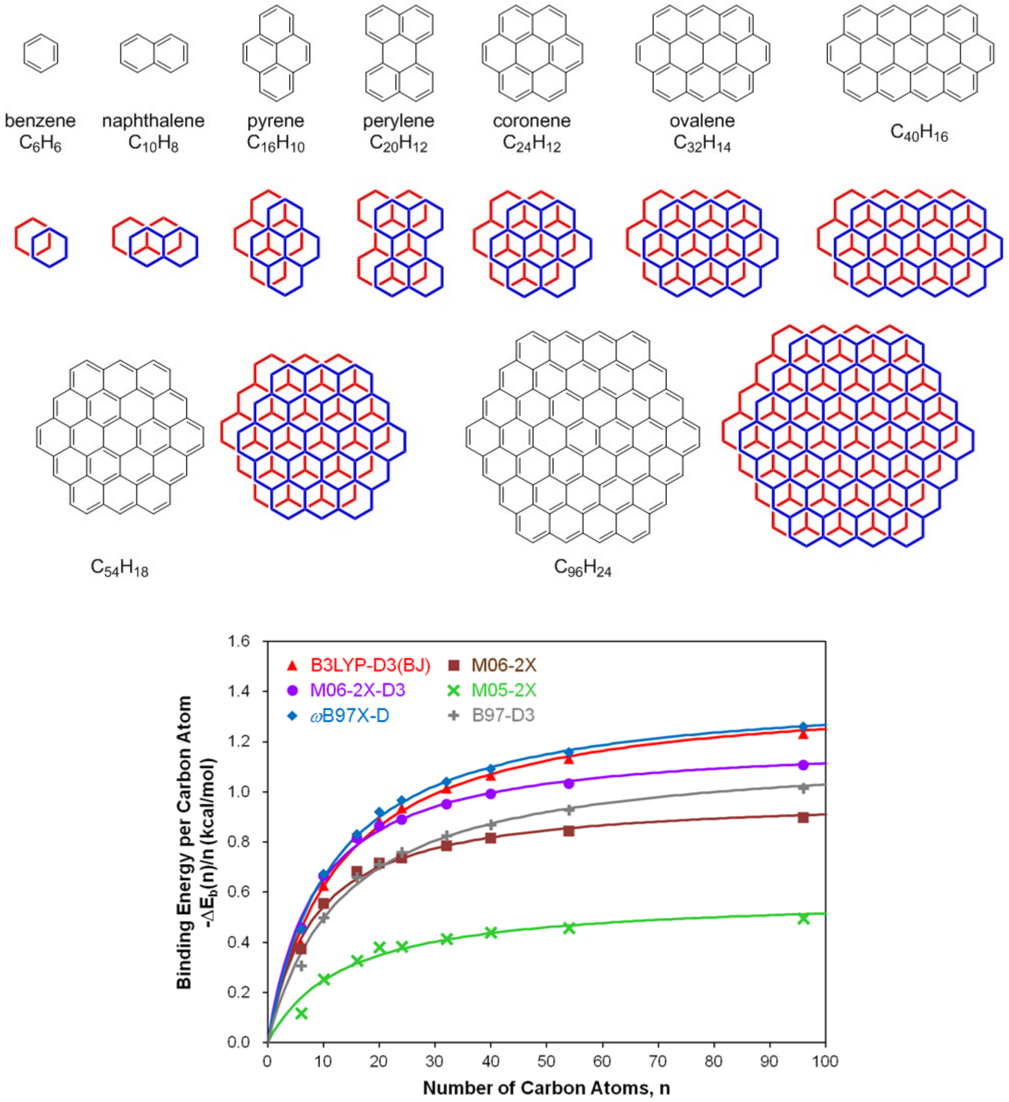


Fig. S2 Binding energy per carbon atom ($-\Delta E_b(n)/n$, in kcal/mol) for the graphene sheet model dimers of the closed-shell systems calculated with different DFT methods. The basis set, except for the B97-D3 functional using the 6-311G(2d,p) level, were calculated at the 6-31+G(d,p)//6-31G(d,p) level. All the nonlinear regression lines fitted from the corresponding nine closed-shell data.

Note: The asymptotic value from the B97-D3/6-311G(2d,p) calculations is 1.17 kcal/mol per carbon atom. This value is in line with the Grimme's paper using B97-D3/TZV(2d,p) level.
(S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104)

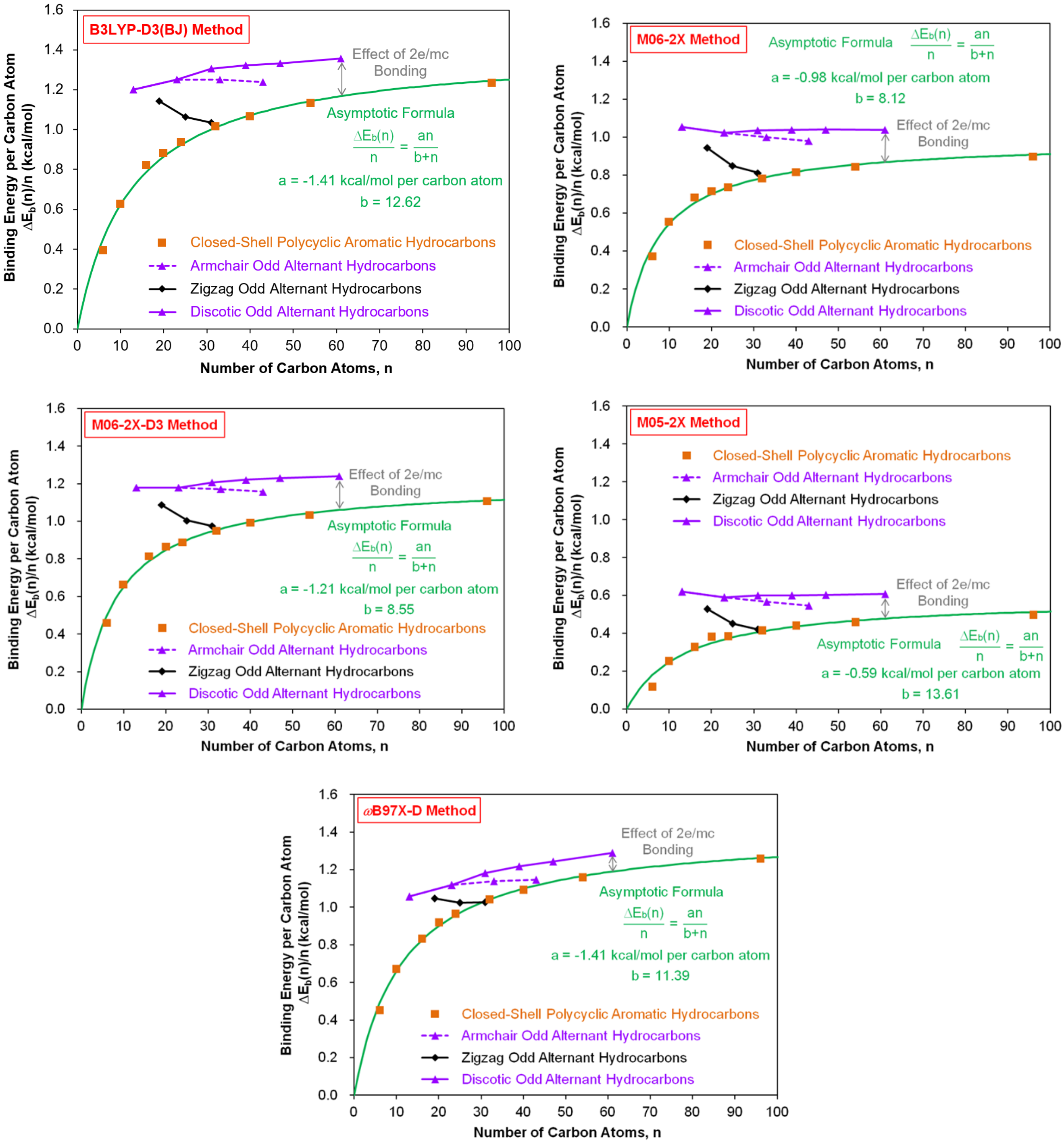
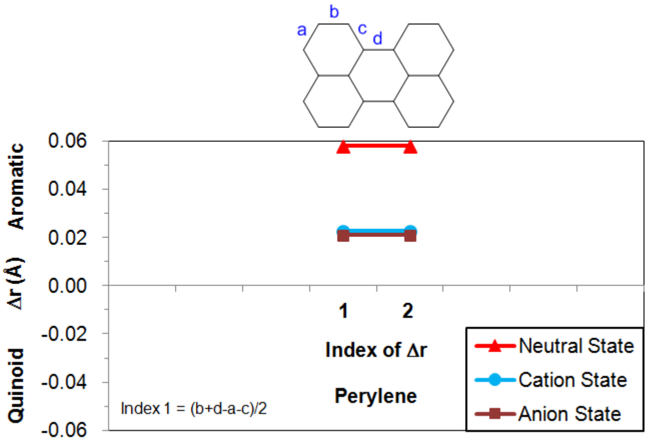
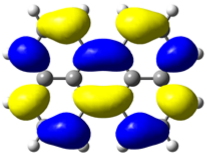
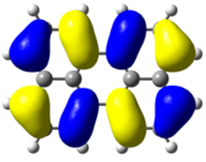


Fig. S3 Binding energy per carbon atom ($\Delta E_b(n)/n$, in kcal/mol) for the graphene sheet model dimers of the closed- and open-shell systems calculated with different DFT methods at the 6-31+G(d,p)//6-31G(d,p) level. All the nonlinear regression lines fitted from the corresponding nine closed-shell data.





LUMO



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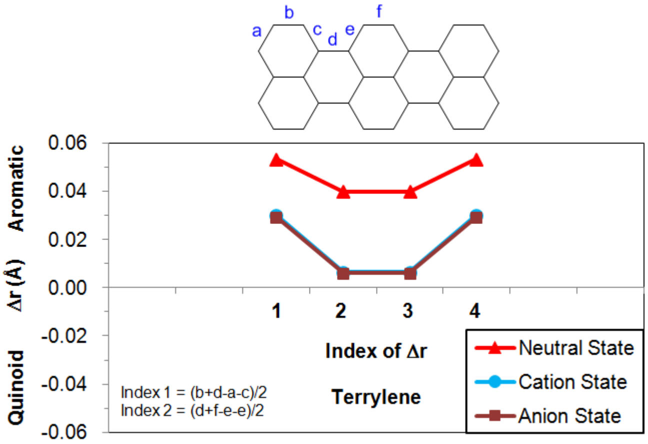

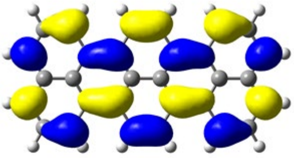

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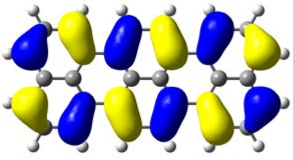

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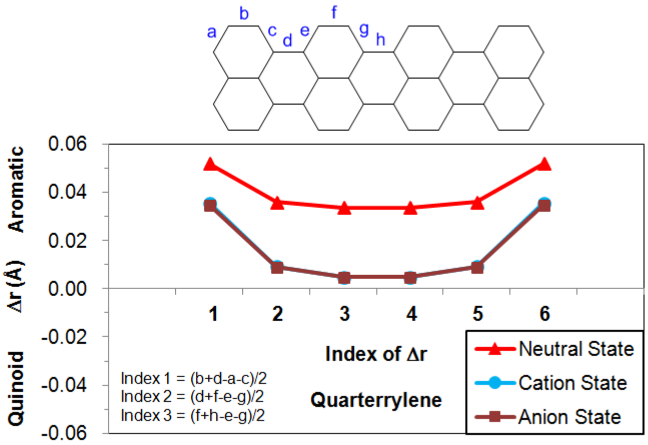

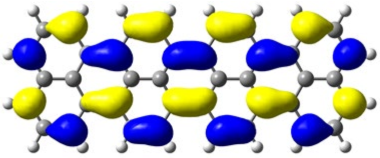

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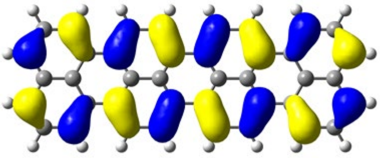

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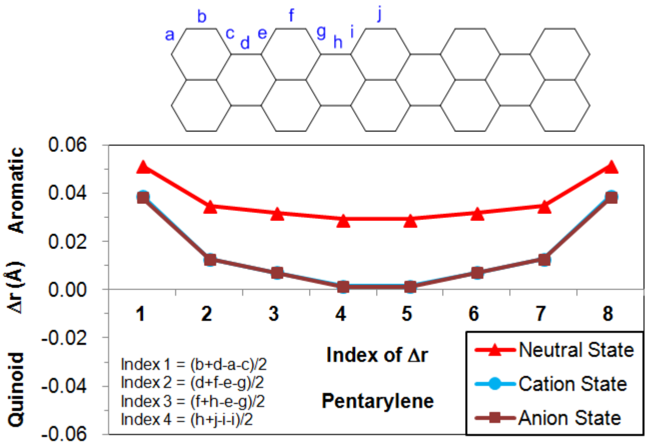

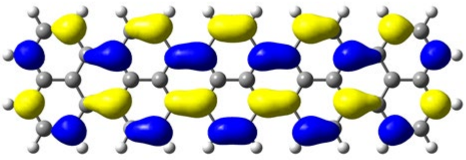

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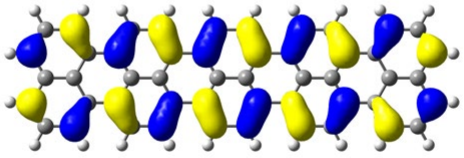
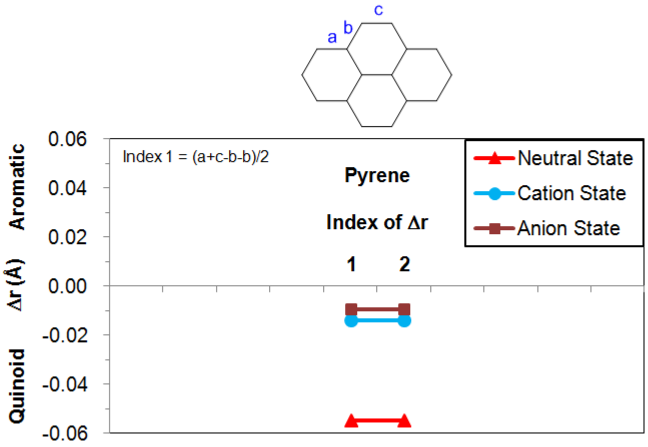
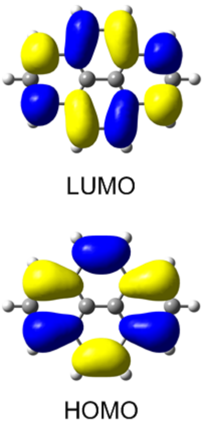
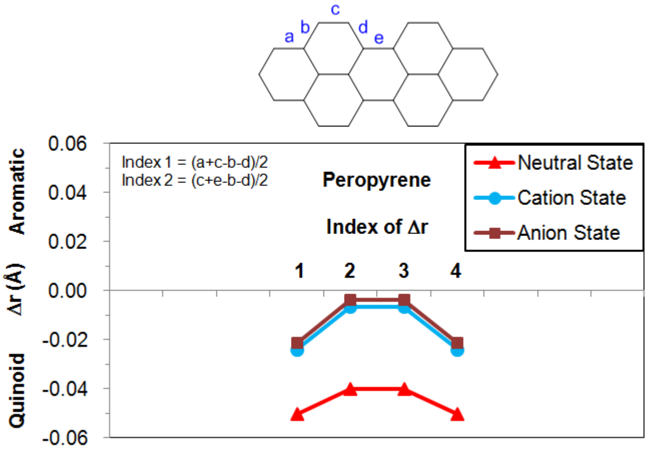


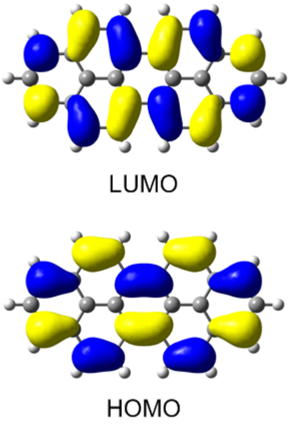
HOMO

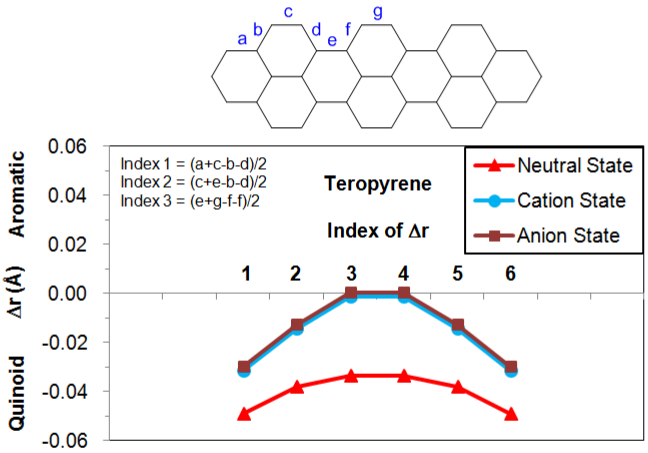
Fig. S4 Bond length alternation parameter (Δr, in Å) and frontier orbitals of the perylene-like PAHs calculated at the B3LYP/6-31G(d,p) level.

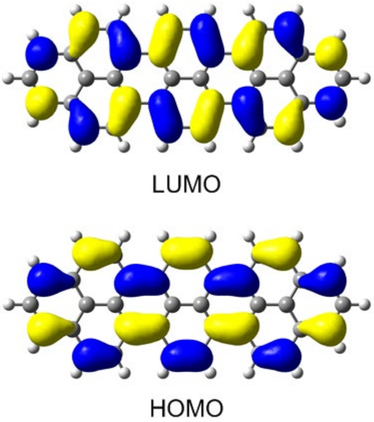

a
b
c
Index 1 = (a+c-b-b)/2
Pyrene
Index of Δr
1
2
Neutral State
Cation State
Anion State
Aromatic
Δr (Å)
Quinoid
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06

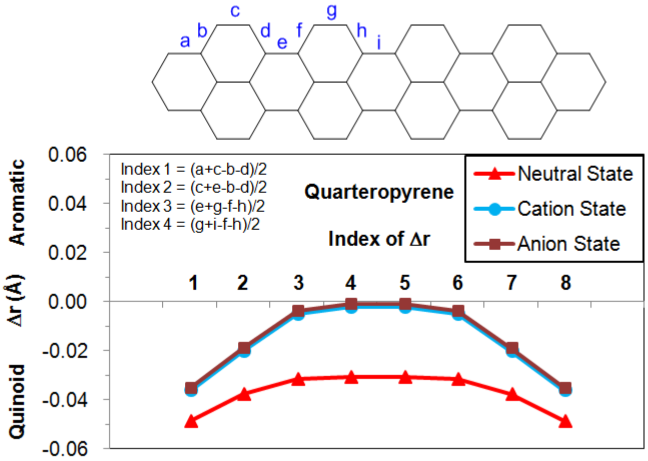

LUMO
HOMO

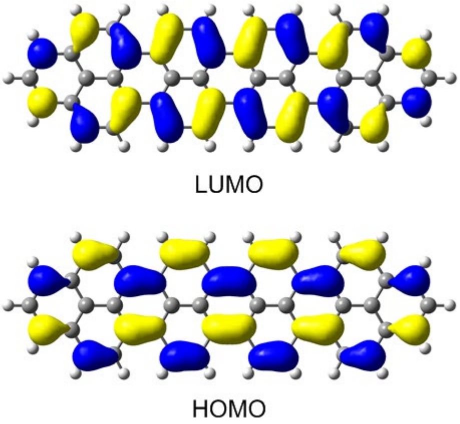

a
b
c
d
e
Index 1 = (a+c-b-d)/2
Index 2 = (c+e-b-d)/2
Peropyrene
Index of Δr
1
2
3
4
Neutral State
Cation State
Anion State
Aromatic
Δr (Å)
Quinoid
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06


LUMO
HOMO


a
b
c
d
e
f
g
Index 1 = (a+c-b-d)/2
Index 2 = (c+e-b-d)/2
Index 3 = (e+g-f-f)/2
Teropyrene
Index of Δr
1
2
3
4
5
6
Neutral State
Cation State
Anion State
Aromatic
Δr (Å)
Quinoid
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06


LUMO
HOMO


a
b
c
d
e
f
g
h
i
Index 1 = (a+c-b-d)/2
Index 2 = (c+e-b-d)/2
Index 3 = (e+g-f-h)/2
Index 4 = (g+i-f-h)/2
Quarteropyrene
Index of Δr
1
2
3
4
5
6
7
8
Neutral State
Cation State
Anion State
Aromatic
Δr (Å)
Quinoid
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06


LUMO
HOMO

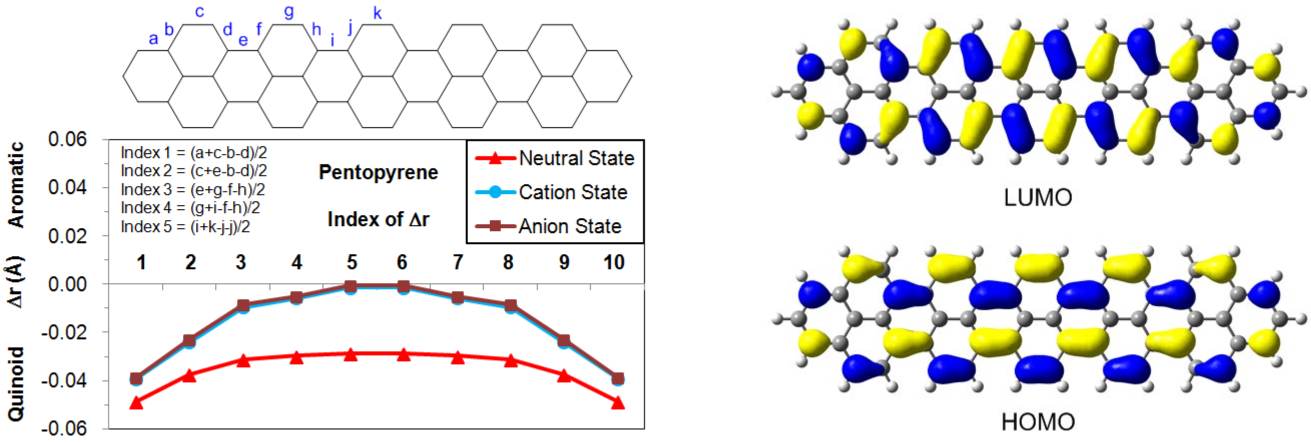


Fig. S5 Bond length alternation parameter (Δr, in Å) and frontier orbitals of the pyrene-like PAHs calculated at the B3LYP/6-31G(d,p) level.

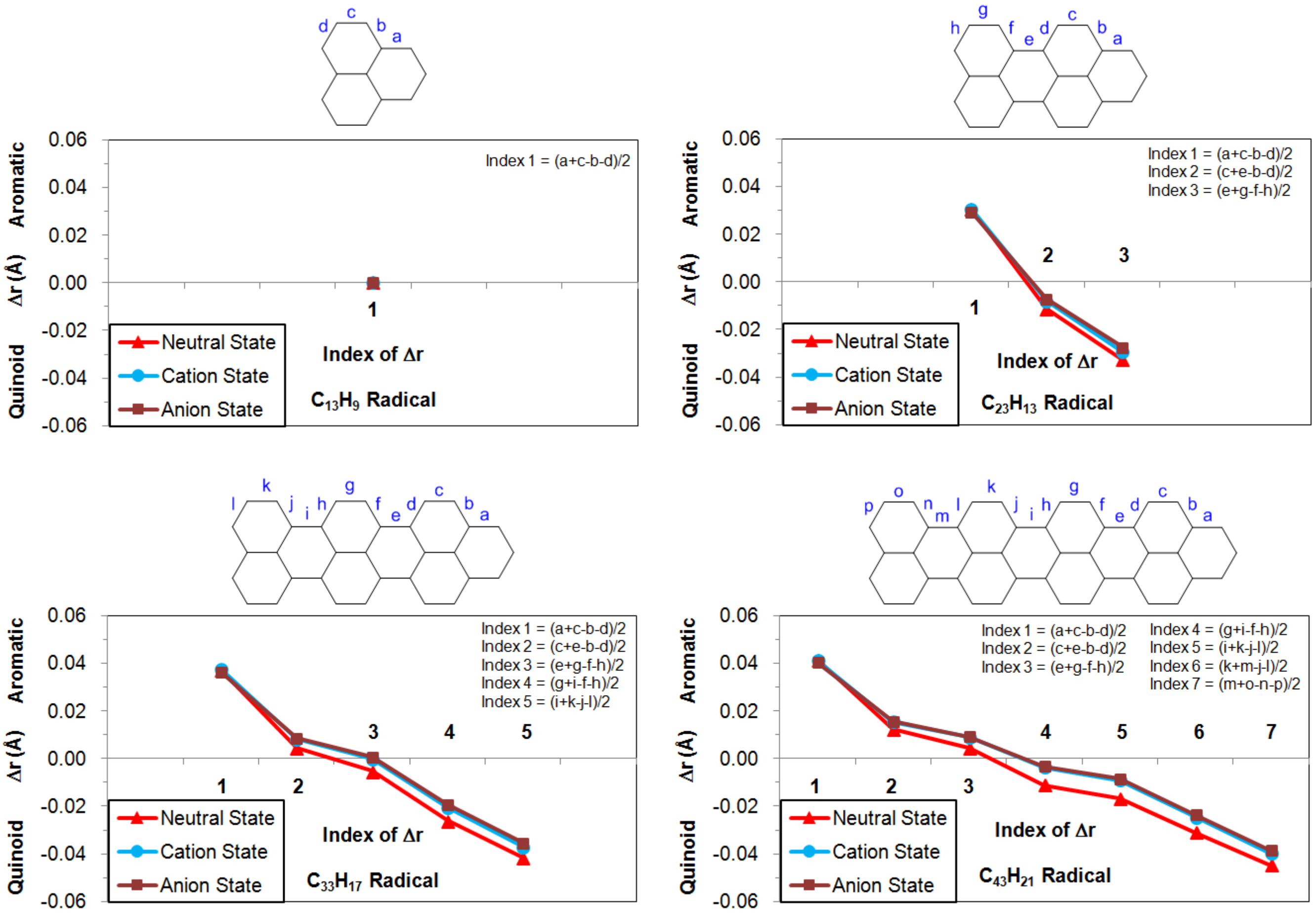


Fig. S6 Bond length alternation parameter (Δr, in Å) of the phenalenyl radical and the armchair odd alternant hydrocarbons calculated at the B3LYP/6-31G(d,p) level.