Multi-Zinc-Expanded Oligoacenes: An Intriguing Class of Well-Defined Open-Shell Singlet Diradicals

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Supporting Information

CONTENTS

1. Additional Computational Details

DFT calculations were performed with the Gaussian 03 program. Throughout optimized calculations, the unrestricted broken symmetry B3LYP method (UB3LYP) with the 6-31G** basis set (for C, H) and SDD (for Zn) was used. Along with geometry optimization, number of electrons outside closed-shell bonding orbitals (BO) and occupation number of LUMO were calculated using CASSCF(10,10)/(6-31G* for C,H and SDD for Zn) method in the HF/(6-31G* for C,H and SDD for Zn) optimized geometry. The diradical index was estimated on the basis of the occupation number of the LUMO, resulting from the CASSCF calculation. Energies for the singlet-triplet gaps ($\Delta E_{(T-OS)}$) were calculated by optimizing both the ground state singlet and excited state triplet electronic configurations using UB3LYP wave functions.

In view of the inconsistent results in producing the ground states of the acenes higher than hexacene, and to give confirmative conclusions for the ground states of them, CCSD(T) correlation method was also employed to clarify if the Zn-modified acenes possess the diradical ground states. Since this kind of calculations are more expensive, only 2Zn-benzene was chosen as representative for UCCSD(T)/(6-31G* for C,H and SDD for Zn) single-point calculations at the UB3LYP/(6-31G** for C,H and SDD for Zn) optimized geometry to get its orbital occupation number and singly occupied molecular orbitals.

In addition, to prove the correctness of the UB3LYP and CASSCF(10,10) results and effect of elongation of the cross-linked C-C bonds on the diradical character, a scan on some parent acenes was also done at the UB3LYP/6-31G(d,p) level with respect to the cross-linked C-C bond with relaxation of other geometrical parameters, and then, the relevant steady points were used for single-point calculations at the UCCSD(T)/6-31G(d,p) level.

Besides, in order to confirm that the unrestricted singlet solutions are the most stable, a comparison with the restricted solutions has been added which is realized through RB3LYP

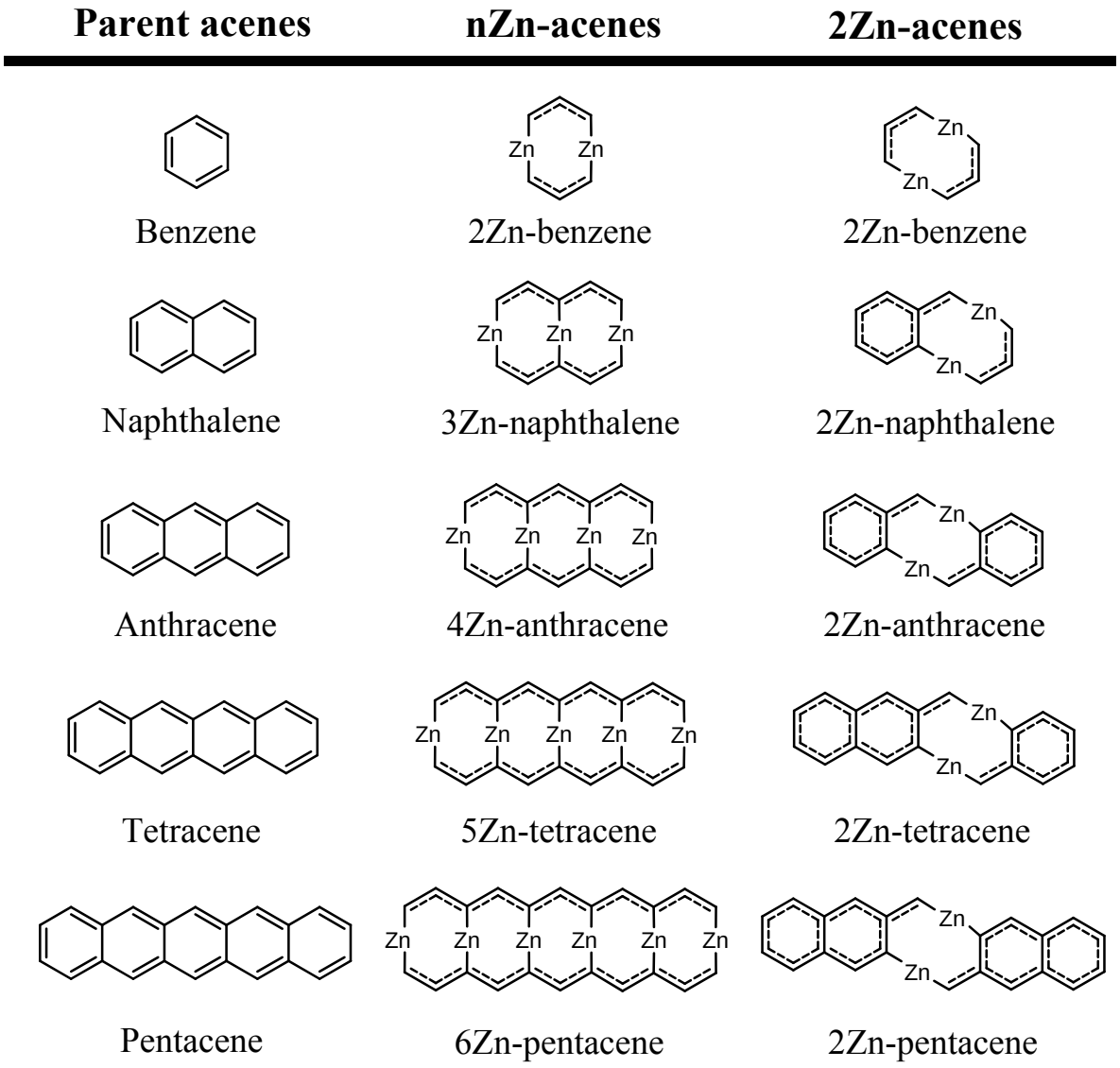
calculation with the same basis set 6-31G** (for C,H) and SDD (for Zn). Followed by this, another CASSCF(10,10) calculation has been performed at the RB3LYP optimal geometries.

At last, we have also proved the correctness of the open-shell singlet diradical character of multi-Zn-expanded acenes in our previous study, through another method called (U)BHandHLYP/(6-31G** for C,H and SDD for Zn), and confirmed the delocalized "aromatic" form of their C-C bonds in each polyacetylene chain by comparison of C-C bond lengths between multi-Zn-expanded acenes and polyacetylene monoradicals which are all obtained by UB3LYP method.

2. Complete ref 19: M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, ; M. A. Robb, J. R. C., J. A. Montgomery, Jr., T. Vreven, ; K. N. Kudin, J. C. B., J. M. Millam, S. S. Iyengar, J. Tomasi, ; V. Barone, B. M., M. Cossi, G. Scalmani, N. Rega, ; G. A. Petersson, H. N., M. Hada, M. Ehara, K. Toyota, ; R. Fukuda, J. H., M. Ishida, T. Nakajima, Y. Honda, O. Kitao, ; H. Nakai, M. K., X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, ; C. Adamo, J. J., R. Gomperts, R. E. Stratmann, O. Yazyev, ; A. J. Austin, R. C., C. Pomelli, J. W. Ochterski, P. Y. Ayala, ; K. Morokuma, G. A. V., P. Salvador, J. J. Dannenberg, ; V. G. Zakrzewski, S. D., A. D. Daniels, M. C. Strain, ; O. Farkas, D. K. M., A. D. Rabuck, K. Raghavachari, ; J. B. Foresman, J. V. O., Q. Cui, A. G. Baboul, S. Clifford, ; J. Cioslowski, B. B. S., G. Liu, A. Liashenko, P. Piskorz, ; I. Komaromi, R. L. M., D. J. Fox, T. Keith, M. A. Al-Laham, ; C. Y. Peng, A. N., M. Challacombe, P. M. W. Gill, ; B. Johnson, W. C., M. W. Wong, C. Gonzalez, and J. A. Pople, ; Gaussian, I., Wallingford CT, 2004.

3. Chart

Chart S1. Two Series of the Designed Multi-Zn-Expanded Acenes and Their Parent Acenes



4. Tables Calculated at the UB3LYP Level

Table S0. Energies (kcal/mol) for the Singlet-Triplet Gaps ($\Delta E_{(T-OS)}$), and Spin Contamination for the Open-Shell Singlet ($<S^2>$) of nZn-acenes and 2Zn-acenes Calculated at the UB3LYP/(6-31G** for C,H and SDD for Zn) Level of Theory

Acenes	$\Delta E_{(T-OS)}$	$<S^2>$	nZn-acenes	$\Delta E_{(T-OS)}$	$<S^2>$	2Zn-acenes	$\Delta E_{(T-OS)}$	$<S^2>$
Benzene	89.47	0.0	2Zn-benzene	2.98	0.93	2Zn-benzene	2.98	0.93
Naphthalene	62.63	0.0	3Zn-naphthalene	2.91	0.94	2Zn-naphthalene	2.08	0.97
Anthracene	41.80	0.0	4Zn-anthracene	2.89	0.94	2Zn-anthracene	0.89	1.02
Tetracene	27.75	0.0	5Zn-tetracene	2.90	0.95	2Zn-tetracene	0.50	1.05
Pentacene	17.94	0.0	6Zn-pentacene	2.92	0.96	2Zn-pentacene	0.25	1.07
Hexacene	10.89	0.0/0.25[a]						
Heptacene	5.70/7.31[a]	0.0/0.80[a]						
Octacene	5.78	1.10				2Zn-octacene	0.18	

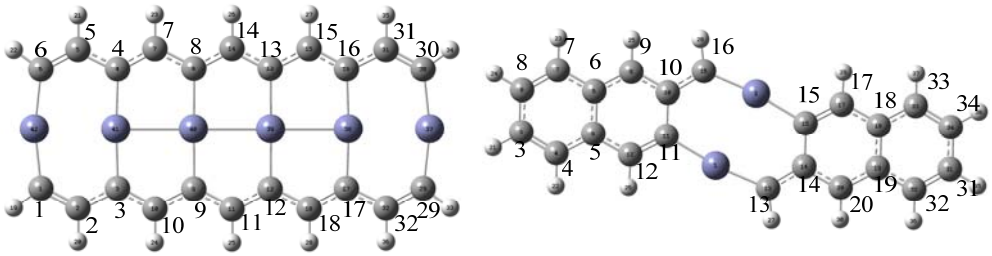
Nonacene	5.33	1.25				2Zn-nonacene	-17.61	
Decacene	5.54	1.41						

[a] calculated at the UB3LYP/6-31G* level. $\Delta E_{(T-OS)}=E_{(T)}-E_{(OS)}$

Table S1. Number of electrons outside closed-shell bonding orbitals (BO) and occupation number of LUMO Calculated using CASSCF(10,10)/(6-31G(d) for C,H and SDD for Zn) method

nZn-polyacene	Total occupancy outside BO	Occupation number of LUMO	2Zn-polyacene	Total occupancy outside BO	Occupation number of LUMO
2Zn-benzene	0.664	0.656	2Zn-benzene	0.664	0.656
3Zn-naphthalene	0.784	0.649	2Zn-naphthalene	0.774	0.689
4Zn-anthracene	0.887	0.675	2Zn-anthracene	0.940	0.813
5Zn-tetracene	1.009	0.733	2Zn-tetracene	1.125	0.880
6Zn-pentacene	1.108	0.734	2Zn-pentacene	1.156	0.932

Table S2. Spin Densities (ρ) on Carbon Atoms and Zinc Atoms of 6Zn-mediated Pentacene and 2Zn-mediated Pentacene Calculated with a Broken-Symmetry UB3LYP/(6-31G** for C,H and SDD for Zn) Method



6Zn-mediated pentacenes/OS		2Zn-mediated pentacenes/OS	
Positions	ρ	positions	ρ
1, 29	-0.246	3	-0.144
2, 32	+0.129	8	+0.082

3, 17	-0.296	4	+0.091
10, 18	+0.181	7	-0.126
9, 12	-0.328	5	-0.151
11	+0.198	6	+0.118
14	-0.198	12	+0.114
8, 13	+0.328	9	-0.368
7, 15	-0.181	11	-0.140
4, 16	+0.296	10	+0.203
5, 31	-0.129	16	-0.674
6, 30	+0.246	13	+0.674
6Zn	0	14	-0.203
		15	+0.140
		20	+0.368
		17	-0.114
		19	-0.118
		18	+0.151
		32	+0.126
		33	-0.091
		31	-0.082
		34	+0.144
		Zn1	+0.064
		Zn2	-0.064

Table S3. Diradical Percentages (%) of Parent Acenes, nZn-acenes and 2Zn-acenes from CASSCF(10/10)/(6-31G(d) for C,H and SDD for Zn) calculations

Parent acenes	Diradical percentage	nZn-acenes	Diradical percentage	2Zn-acenes	Diradical percentage
Benzene [a]	6.5	2Zn-benzene	65.6	2Zn-benzene	65.6
Naphthalene	9.9	3Zn-naphthalene	64.9	2Zn-naphthalene	68.9
Anthracene	13.0	4Zn-anthracene	67.5	2Zn-anthracene	81.3
Tetracene	12.6	5Zn-tetracene	73.3	2Zn-tetracene	88.0
Pentacene	21.4	6Zn-pentacene	73.4	2Zn-pentacene	93.2

[a)] CASSCF(4,4)/6-31G(d)

Table S4. The adiabatic and vertical ionization potentials (AIP, VIP) and the differences (ΔAIP,

ΔVIP) between the Zn-doped and parent acenes (in eV) calculated using B3LYP/C,H/6-311G**//Zn/SDD

Acenes	AIP	VIP	IP^{exp}	AIP (best theor est)	VIP (best theor est)	VIP^{theor} (OVGF)[a]
Benzene	9.09	9.24	9.24378±0.00007	9.22(4)	9.44(8)	9.044
naphthalene	7.82	7.92	8.144±0.001	8.14(1)	8.24(1)	7.847
anthracene	7.04	7.11	7.439±0.006	7.41(9)	7.47(3)	7.202
Tetracene	6.51	6.57	6.97±0.05	6.91(4)	6.94(8)	6.533
pentacene	6.13	6.18	6.63±0.05	6.55(6)	6.57(3)	6.150
Decacene	5.19	5.22				
nZn-acenes	AIP	VIP	2Zn-acenes	AIP	VIP	
2Zn-benzene	6.39	6.44	2Zn-benzene	6.39	6.44	
3Zn-naphthalene	5.91	5.95	2Zn-naphthalene	5.95	6.01	
4Zn-anthracene	5.63	5.66	2Zn-anthracene	5.65	5.68	
5Zn-tetracene	5.44	5.47	2Zn-tetracene	5.45	5.48	
6Zn-pentacene	5.30	5.32	2Zn-pentacene	5.28	5.31	

The values of IP^{exp}, $AIP^{(best\ theor\ est)}$, VIP^{theor}(OVGF), and $VIP^{(best\ theor\ est)}$ of the parent acenes are from ref. Michael Bendikov, Fred Wudl Dmitrii, F. Perepichka *Chem. Rev.* **2004**, *104*, 4891-4945. [a] At OVGF/cc-pVDZ//B3LYP/cc-pVDZ

nZn-acenes	ΔAIP/eV	ΔVIP/eV	2Zn-acenes	ΔAIP/eV	ΔVIP/eV
2Zn-benzene	-2.70	-2.80	2Zn-benzene	-2.70	-2.80
3Zn-naphthalene	-1.91	-1.97	2Zn-naphthalene	-1.87	-1.91
4Zn-anthracene	-1.41	-1.45	2Zn-anthracene	-1.39	-1.43
5Zn-tetracene	-1.07	-1.10	2Zn-tetracene	-1.06	-1.09
6Zn-pentacene	-0.83	-0.86	2Zn-pentacene	-0.85	-0.87

$\Delta AIP = AIP_{(doped)} - AIP_{(initial)}$; $\Delta VIP = VIP_{(doped)} - VIP_{(initial)}$

Table S5. The adiabatic and vertical electron affinities (AEA, VEA) and the differences (ΔAEA, ΔVEA) between the multi-Zn-expanded and parent acenes (in eV) calculated using B3LYP/C,H/6-311G**//Zn/SDD

Acenes	AEA	VEA	Acenes	$EA^{(exp)}$	VEA(OVGF)[a]
Benzene	-1.68	-1.88	benzene	-1.12±0.03	-2.605
naphthalene	-0.42	-0.56	naphthalene	-0.19±0.03	-1.304
anthracene	0.42	0.32	anthracene	0.530±0.005	-0.438
tetracene	1.00	0.92	tetracene	1.04±0.04	+0.158
pentacene	1.42	1.35	pentacene	1.35±0.04	+0.585
nZn-acenes	AEA	VEA	2Zn-acenes	AEA	VEA
2Zn-benzene	1.55	1.52	2Zn-benzene	1.55	1.52
3Zn-naphthalene	1.73	1.70	2Zn-naphthalene	1.74	1.71
4Zn-anthracene	1.89	1.86	2Zn-anthracene	1.95	1.91
5Zn-tetracene	2.02	2.00	2Zn-tetracene	2.16	2.12

6Zn-pentacene	2.14	2.11	2Zn-pentacene	2.32	2.29

The values of $EA^{(exp)}$ and VEA(OVGF) of parent acenes are from ref. Michael Bendikov, Fred Wudl Dmitrii, F. Perepichka *Chem. Rev.* **2004**, *104*, 4891-4945. [a] At OVGF/cc-pVDZ//B3LYP/cc-pVDZ

nZn-acenes	ΔAEA	ΔVEA	2Zn-acenes	ΔAEA	ΔVEA
2Zn-benzene	3.23	3.40	2Zn-benzene	3.23	3.40
3Zn-naphthalene	2.15	2.26	2Zn-naphthalene	2.16	2.27
4Zn-anthracene	1.47	1.54	2Zn-anthracene	1.53	1.59
5Zn-tetracene	1.02	1.08	2Zn-tetracene	1.16	1.20
6Zn-pentacene	0.72	0.76	2Zn-pentacene	0.90	0.94

$\Delta AEA = AEA_{(doped)} - AEA_{(initial)}$; $\Delta VEA = VEA_{(doped)} - VEA_{(initial)}$

Table S6. HOMO-LUMO Gaps of Acenes, nZn-acenes, and 2Zn-acenes

nZn-acenes	Gaps	Acenes	Gaps	2Zn-acenes	Gaps
2Zn-benzene	2.94	Benzene	6.79	2Zn-benzene	2.94
3Zn-naphthalene	2.44	naphthalene	4.82	2Zn-naphthalene	2.49
4Zn-anthracene	2.14	anthracene	3.59	2Zn-anthracene	2.44
5Zn-tetracene	1.94	tetracene	2.78	2Zn-tetracene	2.26
6Zn-pentacene	1.80	pentacene	2.21	2Zn-pentacene	1.15

Table S7. The cross-linked C-C bond distances between two parallel polyacetylene chains (in Å) arranged from left to right

Polyacenes	From left to right
Benzene	1.397, 1.397
Naphthalene	1.417, 1.434, 1.417
Anthracene	1.427, 1.445, 1.445, 1.427
Tetracene	1.431, 1.452, 1.452, 1.452, 1.431
Pentacene	1.433, 1.455, 1.457, 1.457, 1.455, 1.433
Hexacene	1.434, 1.457, 1.460, 1.461, 1.460, 1.457, 1.434
Heptacene	1.435, 1.458, 1.461, 1.463, 1.463, 1.461, 1.458, 1.435
Octacene	1.426, 1.448, 1.455, 1.462, 1.464, 1.462, 1.455, 1.448, 1.426

Table S8. The adjacent Zn-Zn distances of the Zn-modified acenes in open-shell singlet and triplet states (Å)

nZn-polyacene	OS singlet	Triplet	2Zn-polyacene	OS singlet	Triplet
2Zn-benzene	2.887	2.873	2Zn-benzene	2.887	2.873

3Zn-naphthalene	2.698 2.698	2.693 2.693	2Zn-naphthalene	2.837	2.827
4Zn-anthracene	2.667 2.563 2.667	2.663 2.563 2.663	2Zn-anthracene	2.793	2.786
5Zn-tetracene	2.660 2.540 2.540 2.660	2.657 2.540 2.540 2.657	2Zn-tetracene	2.788	2.784
6Zn-pentacene	2.657 2.535 2.518 2.535 2.657	2.655 2.534 2.516 2.534 2.655	2Zn-pentacene	2.784	2.782

Table S9. Calculated Energies (in au), $<S^2>$ Values, and Intramolecular Magnetic Exchange Coupling Constants (J in cm^{-1}) at the UB3LYP/(6-31G** for C,H and SDD for Zn) Level for nZn-polyacene and 2Zn-polyacene.

nZn-acenes	$E_{(T)}$（$<S^2>$）	$E_{(OS)}$（$<S^2>$）	J (cm^{-1})
2Zn-benzene	-686.3977909（2.053）	-686.4025393（0.933）	-930.4
3Zn-naphthalene	-1067.1476712（2.083）	-1067.1523121（0.936）	-888.1
4Zn-anthracene	-1447.8913324（2.112）	-1447.8959416（0.941）	-864.3
5Zn-tetracene	-1828.6325033（2.141）	-1828.6371265（0.949）	-851.3
6Zn-pentacene	-2209.3722450（2.171）	-2209.3769041（0.959）	-843.9
2Zn-acenes	$E_{(T)}$（$<S^2>$）	$E_{(OS)}$（$<S^2>$）	J(cm^{-1})
2Zn-benzene	-686.3977909（2.053）	-686.4025393（0.933）	-930.4
2Zn-naphthalene	-840.0504831（2.054）	-840.0538043（0.966）	-670.3
2Zn-anthracene	-993.7035955（2.054）	-993.7050163（1.022）	-302.1
2Zn-tetracene	-1147.3496103（2.060）	-1147.3504103（1.049）	-173.6
2Zn-pentacene	-1300.9955381（2.067）	-1300.9959387（1.069）	-88.1

5. Figures for the Geometries, SOMOs and Spin Density Distributions of All Zn-Modified Acene Derivatives

Results for other nZn-acenes

1） 2Zn-benzene

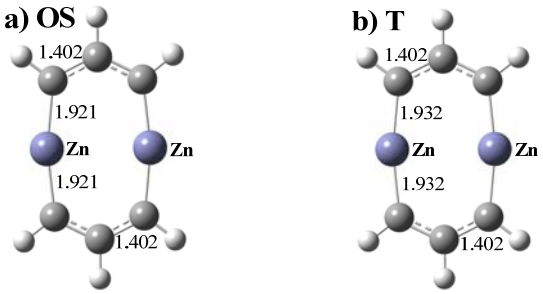


Fig S1. Optimized geometries with indicated bond lengths (Å) for 2Zn-benzene(a. open-shell singlet; b. triplet).

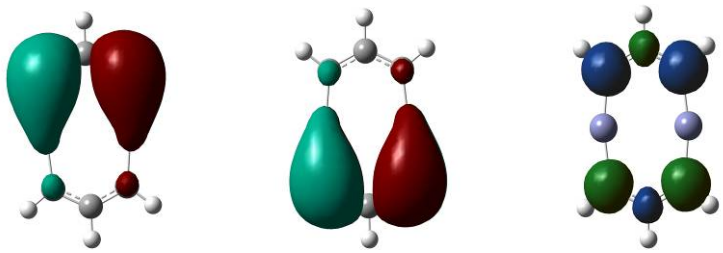


Fig S2. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 2Zn-benzene.

2） 3Zn-naphthalene

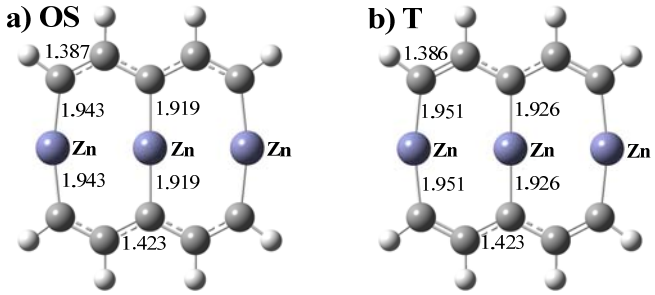


Fig S3. Optimized geometries with indicated bond lengths (Å) for 3Zn-naphthalene (a. open-shell singlet; b. triplet).

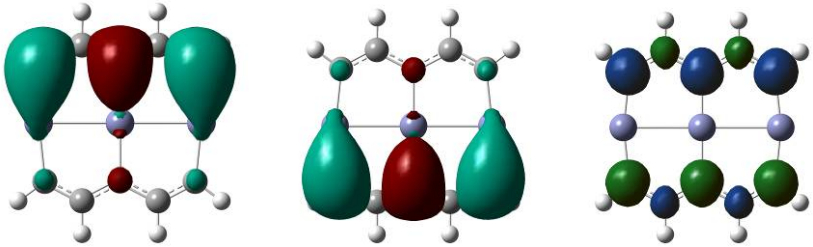


Fig S4. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 3Zn-naphthalene.

3) 4Zn-anthracene

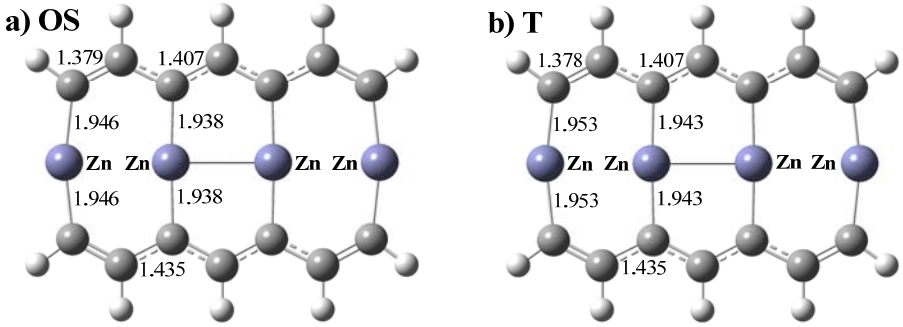


Fig S5. Optimized geometries with indicated bond lengths (Å) for 4Zn-anthracene (a. open-shell singlet; b. triplet).

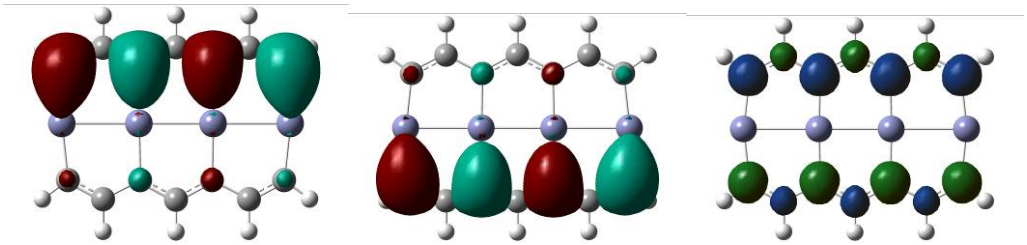


Fig S6. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 4Zn-anthracene.

4) 5Zn-tetracene

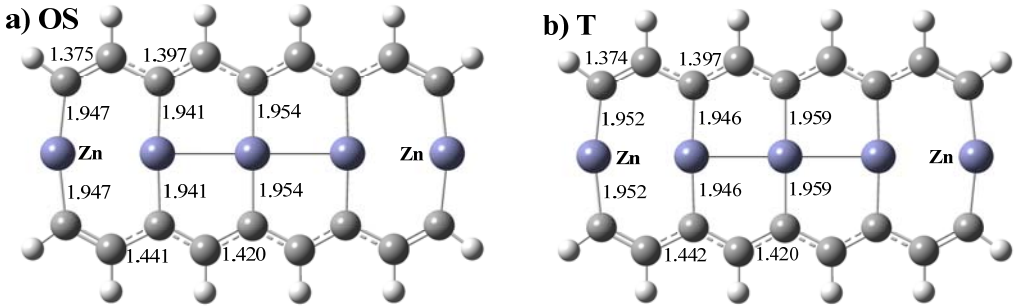


Fig S7. Optimized geometries with indicated bond lengths (Å) for 5Zn-tetracene (a. open-shell singlet; b. triplet).

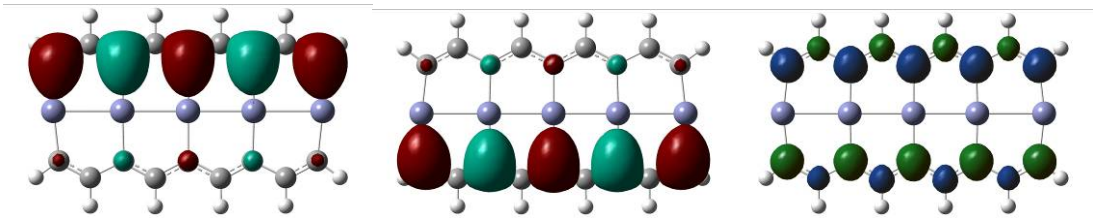


Fig S8. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 5Zn-tetracene.

Results for other 2Zn-polyacenes

1) 2Zn-benzene

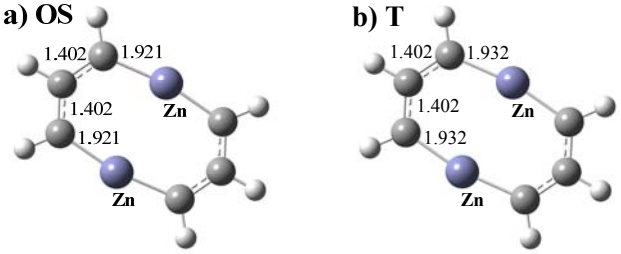


Fig S9. Optimized geometries with indicated bond lengths (Å) for 2Zn-benzene(a. open-shell

singlet; b. triplet).

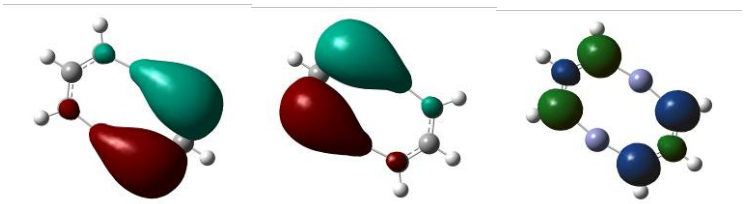


Fig S10. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 2Zn-benzene.

2) 2Zn-naphthalene

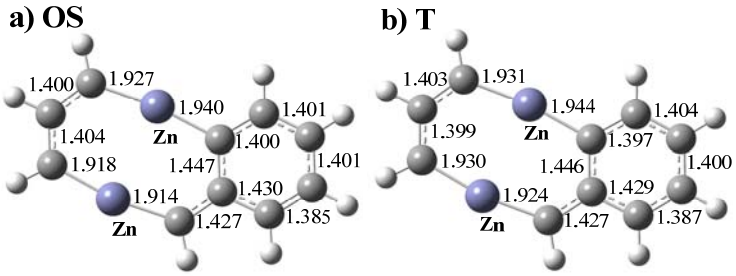


Fig S11. Optimized geometries with indicated bond lengths (Å) for 2Zn-naphthalene (a. open-shell singlet; b. triplet).

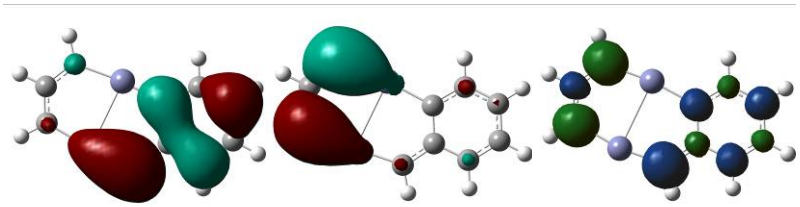


Fig S12. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 2Zn-naphthalene.

3) 2Zn-anthracene

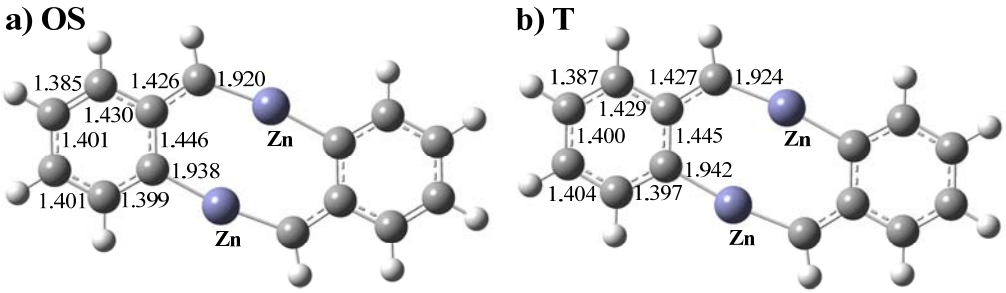


Fig S13. Optimized geometries with indicated bond lengths (Å) for 2Zn-anthracene (a.

open-shell singlet; b. triplet).

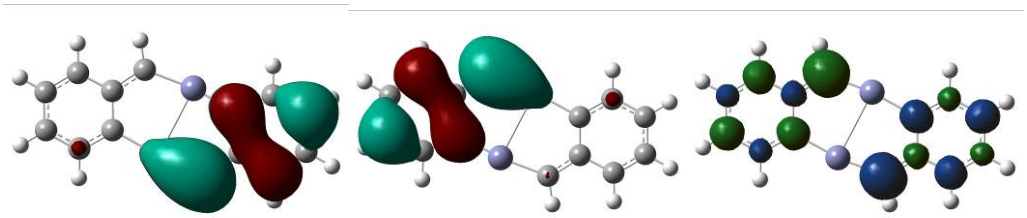


Fig S14. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 2Zn-anthracene.

4) 2Zn-tetracene

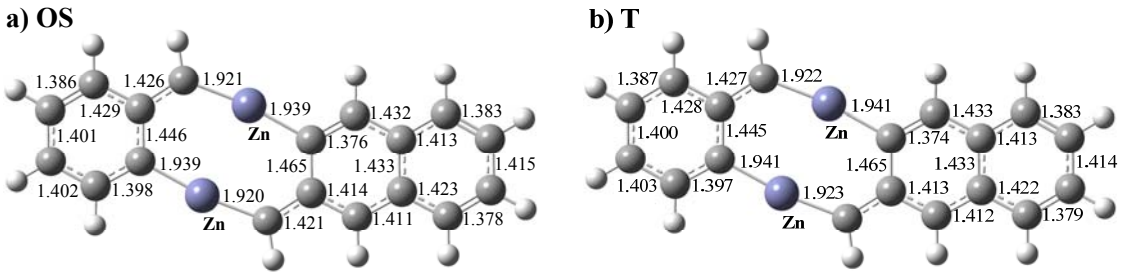


Fig S15. Optimized geometries with indicated bond lengths (Å) for 2Zn-tetracene (a. open-shell singlet; b. triplet).

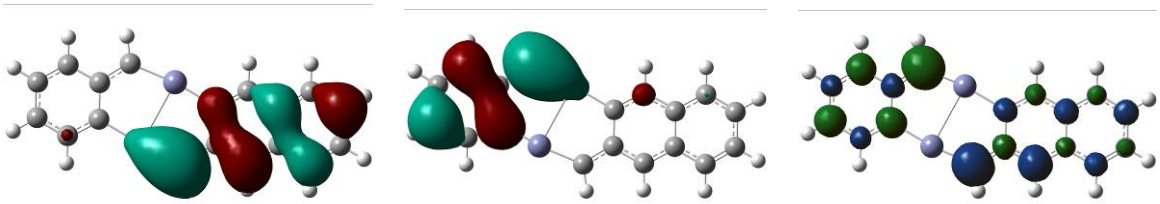


Fig S16. SOMOs (the former two) and spin density map (the last one) for open-shell singlet 2Zn-tetracene.

6. Additional Tables and Figures Calculated at the UCCSD(T)//UB3LYP Level with Same Basis Sets as Those Used for the above UB3LYP Calculations As A Confirmation of Our UB3LYP and CASSCF-Based Conclusions

Table S10. Spin Contamination for the Open-Shell Singlet (<S^2>), Number of Electrons Outside

Closed-shell Bonding Orbitals (BO), Occupation Number of LUMO and Diradical Percentages (%) of 2Zn-benzene Calculated at the UCCSD(T)/(6-31G* for C,H and SDD for Zn) Level of Theory in the UB3LYP/(6-31G** for C,H and SDD for Zn) optimized geometry. The corresponding figure is given Figure S17.

Molecule	$<S^2>$	Total occupancy outside BO	Occupation number of LUMO	Diradical percentage/%
2Zn-benzene	1.41	1.109	0.897	89.7

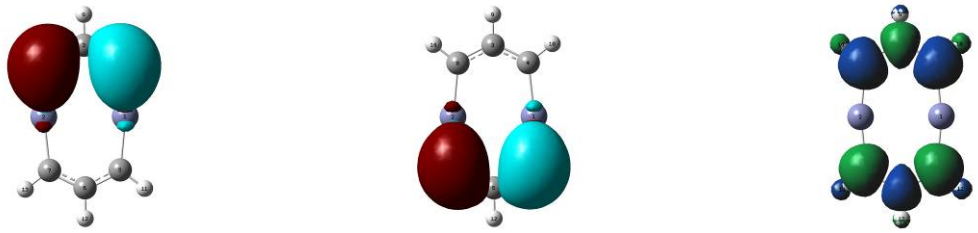


Figure S17. SOMOs (the former two, isovalue = 0.02) and spin density map (the last one) for open-shell singlet 2Zn-benzene (isovalue = 0.004).

Table S11. The Cross-linked C-C Bond Distances (in Å), Number of Electrons Outside Closed-shell Bonding Orbitals (BO), Occupation Number of LUMO and Diradical Percentages (%) of Three Representative Elongated Parent Acenes Calculated at the UCCSD(T)/6-31G(d,p) [a] Level of Theory.

Elongated Parent Acenes	Cross-linked C-C Bond Distances / Å	Total Occupancy Outside BO	Occupation Number of LUMO	Diradical Percentage / %
Benzene	1.597, 1.597	0.533	0.342	34.2

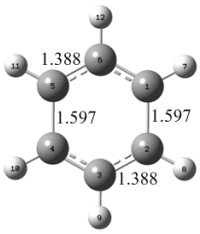
		0.193[b] 0[c]	0.123[b] 0[c]	12.3[b] 0[c]
Benzene	1.797, 1.797	0.783 0.296[b] 0.002[c]	0.547 0.217[b] 0.002[c]	54.7 21.7[b] 0.2[c]
Benzene	1.997, 1.997	1.084 0.463[b] 0.265[c]	0.699 0.292[b] 0.247[c]	69.9 29.2[b] 24.7[c]
Benzene	2.197, 2.197	1.564 0.678[b] 0.528[c]	0.801 0.436[b] 0.483[c]	80.1 43.6[b] 48.3[c]
Acene Chain Axial Direction	**Cross-linked C-C Bond Distances / Å**	**Total Occupancy Outside BO**	**Occupation Number of LUMO**	**Diradical Percentage / %**
Anthracene	1.627, 1.645, 1.645, 1.627	0	0	0
Anthracene	1.827, 1.845, 1.845, 1.827	1.246	0.564	56.4
Single Ring Quasi Transversal Direction	**Cross-linked C-C Bond Distances / Å**	**Total Occupancy Outside BO**	**Occupation Number of LUMO**	**Diradical Percentage / %**
Anthracene	1.601, 1.601	1.138	0.577	57.7
Anthracene	1.801, 1.801	1.297	0.714	71.4

[a] The UCCSD(T)/6-31G(d,p) single-point calculated results at the UB3LYP/6-31G(d,p) for scan-relaxed geometries. [b] The CASSCF(6,6)/6-31G(d,p)//HF/6-31G(d) reults. [c] The UB3LYP/6-31G(d, p) results.

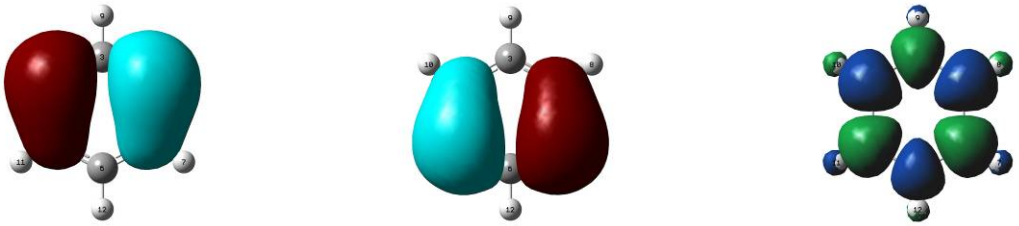
Figures: (The UCCSD(T)/6-31G(d,p) single-point calculated results at the UB3LYP/6-31G(d,p) for scan-relaxed geometries**)**

1) Elongated benzene (open-shell singlet)

a) 1.597 Å of the cross-linked C-C bond distances

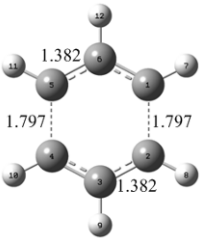


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated benzene whose cross-linked C-C bond distances are fixed at 1.597 Å.

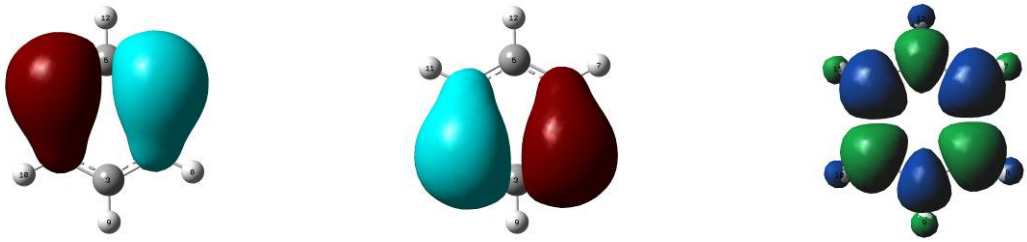


SOMOs (the former two) and spin density map (the last one) for open-shell singlet elongated benzene.

b) 1.797 Å of the cross-linked C-C bond distances

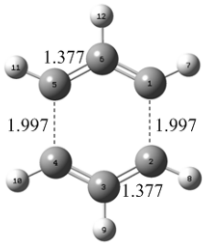


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated benzene whose cross-linked C-C bond distances are fixed at 1.797 Å.

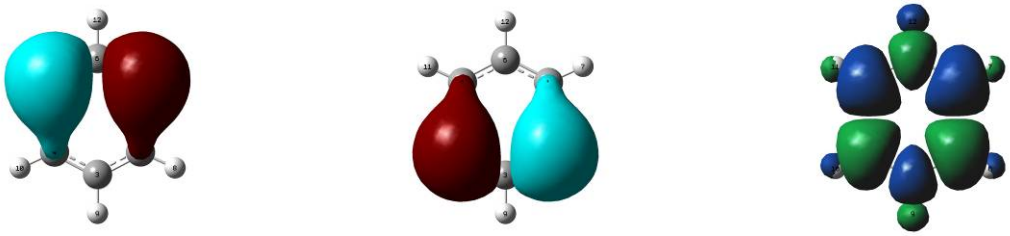


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated benzene whose cross-linked C-C bond distances are fixed at 1.797 Å.

c) 1.997 Å of the cross-linked C-C bond distances

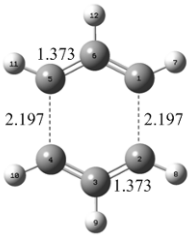


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated benzene whose cross-linked C-C bond distances are fixed at 1.997 Å.

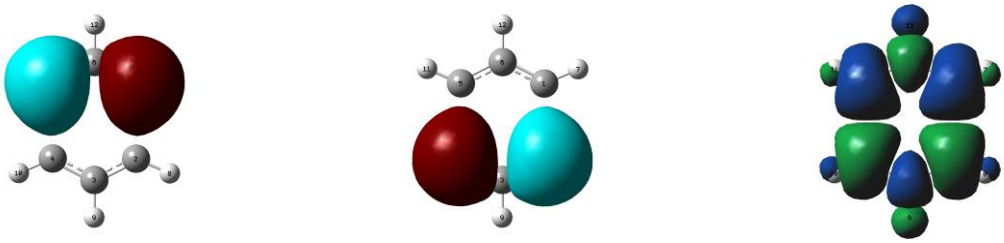


SOMOs (the former two) and spin density map (the last one) for open-shell singlet elongated benzene.

d) 2.197 Å of the cross-linked C-C bond distances

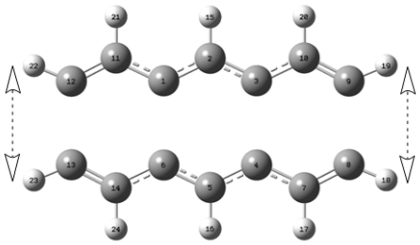


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated benzene whose cross-linked C-C bond distances are fixed at 2.197 Å.

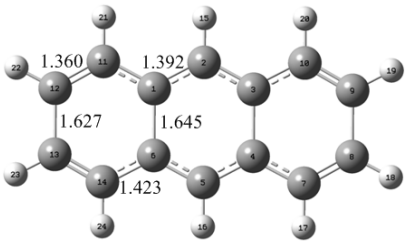


SOMOs (the former two) and spin density map (the last one) for open-shell singlet elongated benzene.

2) Elongated Anthracene (Acene Chain Axial Direction, Open-Shell Singlet)

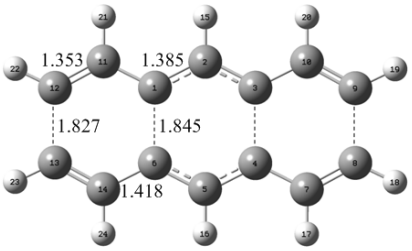


a) 1.627 and 1.645 Å of the cross-linked C-C bond distances (with no diradical character)

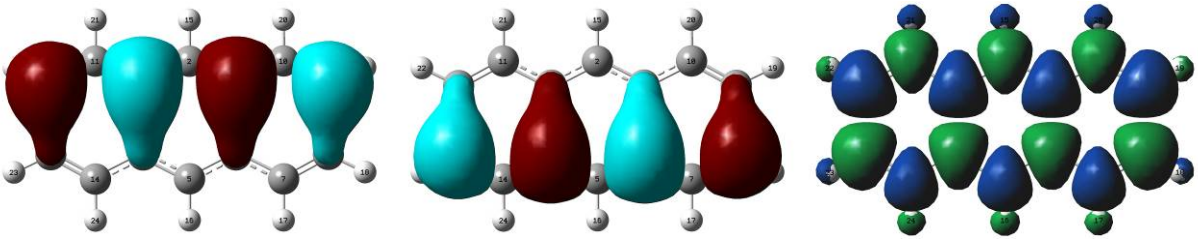


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated anthracene (acene chain axial direction) whose cross-linked C-C bond distances are fixed at 1.627, 1.645, 1.645, 1.627 Å, respectively.

b) 1.827 and 1.845 Å of the cross-linked C-C bond distances

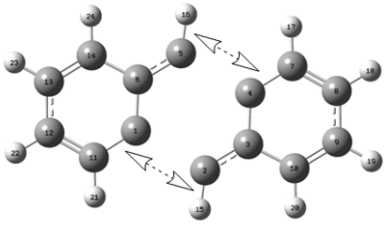


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated anthracene (acene chain axial direction) whose cross-linked C-C bond distances are fixed at 1.827, 1.845, 1.845, 1.827 Å, respectively.

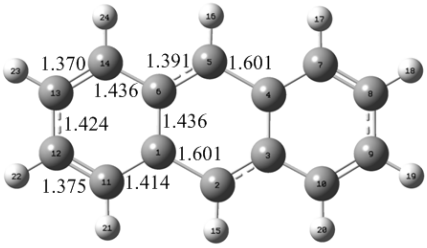


SOMOs (the former two) and spin density map (the last one) for open-shell singlet elongated anthracene (acene chain axial direction).

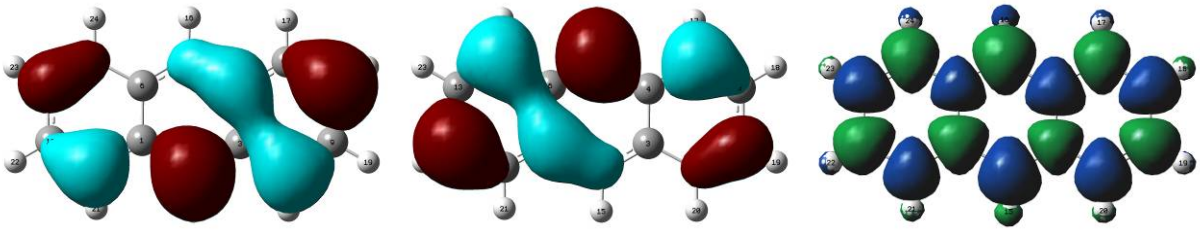
3) Elongated Anthracene (Single Ring Quasi-Transversal Direction)



a) 1.601 Å of the cross-linked C-C bond distances

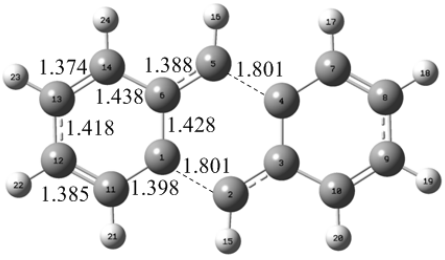


Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated anthracene (single ring quasi transversal direction) whose cross-linked C-C bond distances are fixed at 1.601 Å.

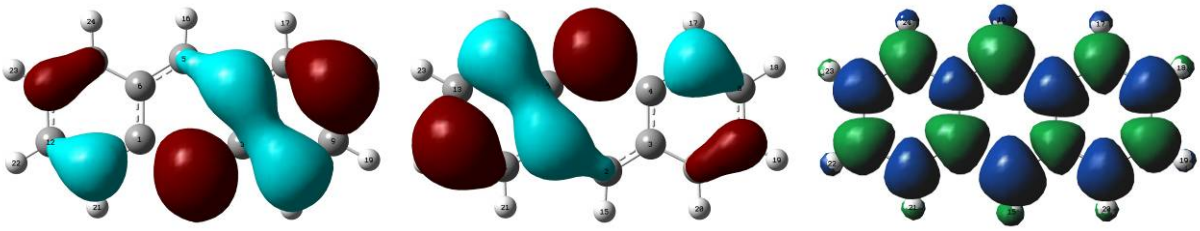


SOMOs (the former two) and spin density map (the last one) for open-shell singlet elongated anthracene (single ring quasi transversal direction).

b) 1.801 Å of the cross-linked C-C bond distances



Optimized geometries with indicated bond lengths (Å) for open-shell singlet elongated anthracene (single ring quasi transversal direction) whose cross-linked C-C bond distances are fixed at 1.801 Å.



SOMOs (the former two) and spin density map (the last one) for open-shell singlet elongated anthracene (single ring quasi transversal direction).

7. New Additional Tables and Figures Calculated at the (U)BHandHLYP//CASSCF Methods with the Same Basis Sets as Those Used for the Previous UB3LYP Calculations As A Confirmation of Our Former UB3LYP and CASSCF-Based Conclusions

Table S12. Energies (kcal/mol) for the Singlet-Triplet Gaps ($\Delta E_{(T-OS)}$), Spin Contamination for the Open-Shell Singlet ($<S^2>$), Differences between Open-Shell Broken-Symmetry Singlet and Closed-Shell RBHandHLYP Solution $\Delta E_{(OS-CS)}$ of nZn-acenes and 2Zn-acenes Calculated at the (U)BHandHLYP/(6-31G** for C,H and SDD for Zn) Level of Theory [a]

nZn-acenes	$\Delta E_{(T-OS)}$	$<S^2>$	$\Delta E_{(OS-CS)}$	2Zn-acenes	$\Delta E_{(T-OS)}$	$<S^2>$	$\Delta E_{(OS-CS)}$
2Zn-benzene	1.92	1.08	-27.15	2Zn-benzene	1.92	1.08	-27.15
3Zn-naphthalene	1.83	1.18	-24.00	2Zn-naphthalene	1.40	1.12	-28.16
4Zn-anthracene	1.79	1.30	-22.65	2Zn-anthracene	0.72	1.17	-31.29
5Zn-tetracene	1.79	1.44	-22.16	2Zn-tetracene	0.52	1.22	-33.79
6Zn-pentacene	1.82	1.61	-22.21	2Zn-pentacene	0.39	1.27	-36.56

[a] **Notes:** $\Delta E_{(T-OS)}=E_{(T)}-E_{(OS)}$, and $\Delta E_{(OS-CS)}=E_{(OS)}-E_{(CS)}$

Table S13. Number of electrons outside closed-shell bonding orbitals (BO), occupation number of LUMO, and Diradical Percentages (%) Calculated using CASSCF(10,10)/(6-31G(d) for C,H and SDD for Zn) method performed at the RB3LYP(6-31G** for C,H and SDD for Zn) optimal geometries.

nZn-polyacenes	Total occupancies outside BO	Occupation numbers of LUMO	Diradical percentages
2Zn-benzene	0.833	0.705	70.5
3Zn-naphthalene	0.908	0.719	71.9
4Zn-anthracene	0.872	0.675	67.5
5Zn-tetracene	0.847	0.668	66.8
6Zn-pentacene	0.986	0.709	70.9
2Zn-benzene	0.833	0.705	70.5
2Zn-naphthalene	1.161	0.811	81.1
2Zn-anthracene	1.169	0.872	87.2
2Zn-tetracene	1.052	0.912	91.2
2Zn-pentacene	1.210	0.970	97.0

Table S14. The C-C bond distances of two parallel polyacetylene chains (in Å) in molecules of polyacenes, polyacetylene radicals and Zn-modified acenes (arranged from left to right).

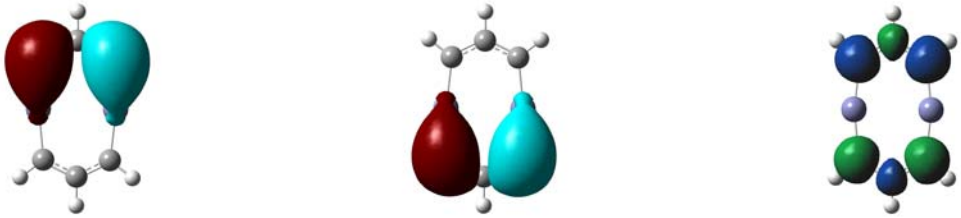
Polyacene	From left to right	Polyacetylene radical	From left to right	nZn-polyacene	From left to right
Benzene	1.397 1.397	$CH_2(CH)CH_2$	1.336 1.470	2Zn-benzene	1.402 1.402
Naphthalene	1.376 1.421 1.421 1.376	$CH_2(CH)_3CH_2$	1.340 1.456 1.346 1.467	3Zn-naphthalene	1.387 1.423 1.423 1.387
Anthracene	1.370 1.430 1.401 1.401 1.430 1.370	$CH_2(CH)_5CH_2$	1.357 1.426 1.392 1.392 1.426 1.357	4Zn-anthracene	1.379 1.435 1.407 1.407 1.435 1.379
Tetracene	1.367 1.434 1.393 1.410 1.410 1.393 1.434	$CH_2(CH)_7CH_2$	1.344 1.447 1.356 1.440 1.356 1.445 1.350	5Zn-tetracene	1.375 1.441 1.397 1.420 1.420 1.397 1.441

	1.367		1.466		1.375
Pentacene	1.365 1.436 1.389 1.415 1.402 1.402 1.415 1.389 1.436 1.365	$CH_2(CH)_9CH_2$	1.351 1.435 1.375 1.412 1.393 1.393 1.412 1.375 1.435 1.351	6Zn-pentacene	1.373 1.445 1.391 1.428 1.410 1.410 1.428 1.391 1.445 1.373

Figures for SOMOs and Spin Density Distributions of All Zn-Modified Acene Derivatives Calculated at the UBHandHLYP/(6-31G for C,H and SDD for Zn) Level of Theory**

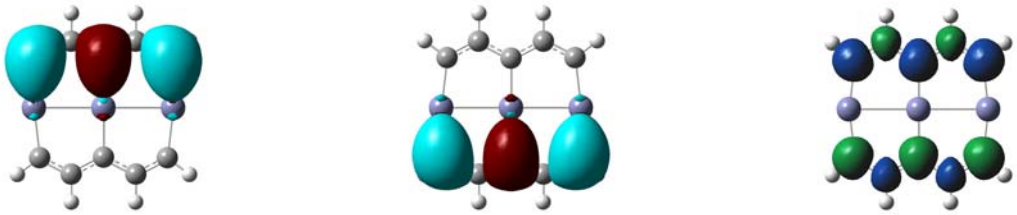
Results for other nZn-acenes

1) 2Zn-benzene



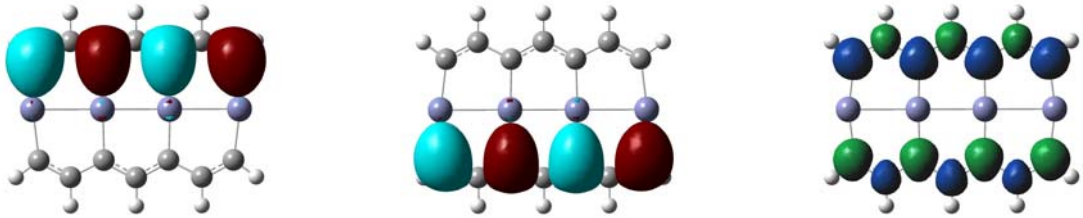
SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 2Zn-benzene.

2) 3Zn-naphthalene



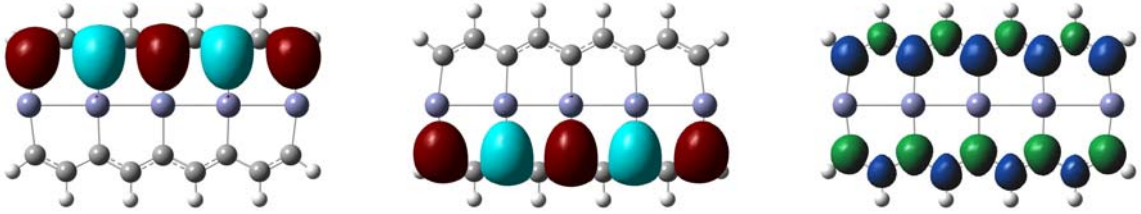
SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 3Zn-naphthalene.

3) 4Zn-anthracene



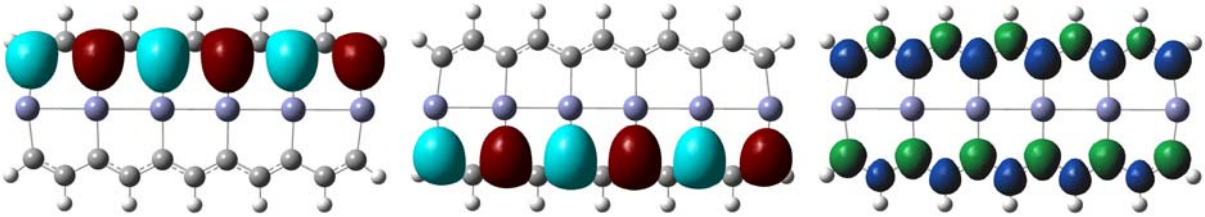
SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 4Zn-anthracene.

4) 5Zn-tetracene



SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 5Zn-tetracene.

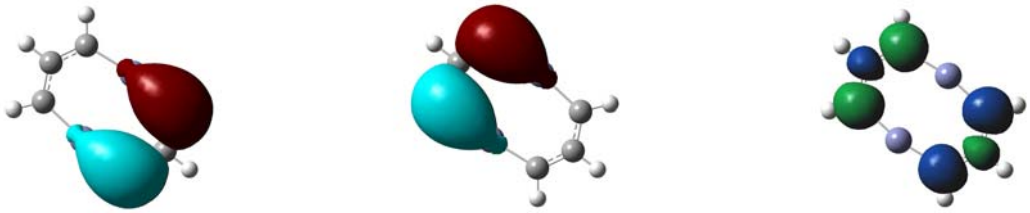
5) 6Zn-pentacene



SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 6Zn-pentacene.

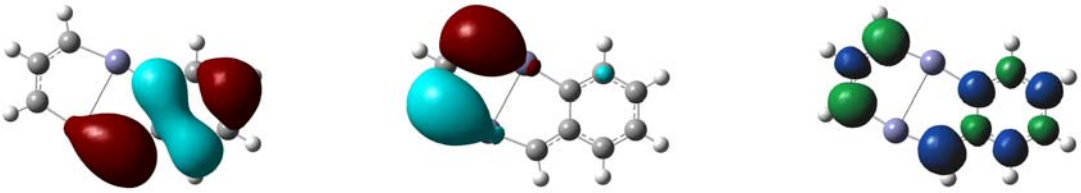
Results for other 2Zn-acenes

1) 2Zn-benzene



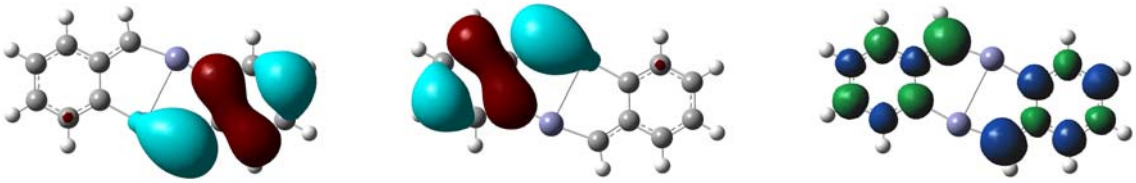
SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 2Zn-benzene.

2) 2Zn-naphthalene



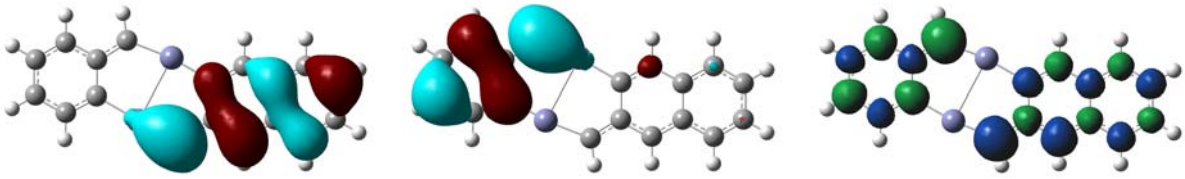
SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 2Zn-naphthalene.

3) 2Zn-anthracene



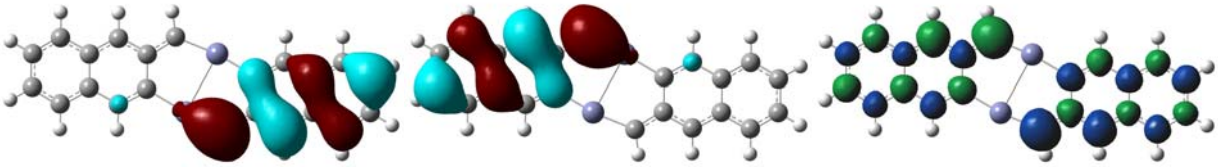
SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 2Zn-anthracene.

4) 2Zn-tetracene



SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 2Zn-tetracene.

5) 2Zn-pentacene



SOMOs (the former two, isovalue = 0.02) and spin density map (the last one, isovalue = 0.004) for open-shell singlet 2Zn-pentacene.