Remarkable Magnetic Coupling Interactions in Multi-Beryllium-Expanded Small Graphene-Like Molecules with Well-Defined Polyradical Characters

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Supporting Information

Contents

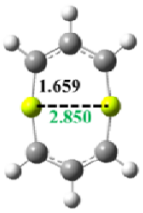
1. Relevant Data for Describing the Ground States of All Molecules

Table S1. The calculated energies (in au) of the closed-shell singlet (CS), broken-symmetry open-shell singlet (BS) and triplet (T) and the corresponding energy orders at the (U)B3LYP/6-311++G (d,p) level.

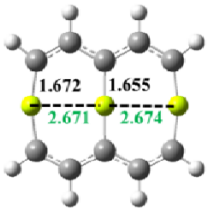
(n+1)Be-nA	**$E_{(CS)}$**	**$E_{(BS)}$**	**$E_{(T)}$**
2Be-1A	-261.7117584	-261.721268	-261.7130934
3Be-2A	-430.1276823	-430.1330716	-430.1239735
2Be-nA	**$E_{(CS)}$**	**$E_{(BS)}$**	**$E_{(T)}$**
2Be-1A	-261.7117584	-261.721268	-261.7130934
2Be-2A	-415.3954058	-415.4062144	-415.4003519
2Be-3A	-569.0762966	-569.0908887	-569.0882223
2Be-4A	-722.7517665	-722.7696919	-722.7682185
2Be-5A	-876.4268885	-876.4487565	-876.4480721
3Be-GP	**$E_{(CS)}$**	**$E_{(BS)}$**	**$E_{(T)}$**
3Be-Ant	-889.9828263	-889.9954974	-889.9930259
3Be-Bpe	-889.9906375	-889.9975095	-889.9902332

2. All Optimized Molecular Geometries of Multi-Be-Expanded Oligoacenes

(n+1)Be-nA series:

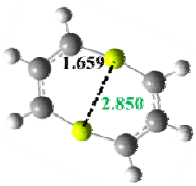


2Be-1A-BS

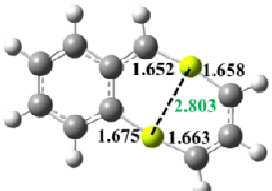


3Be-2A-BS

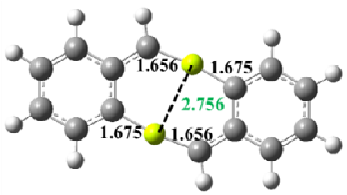
2Be-nA series:



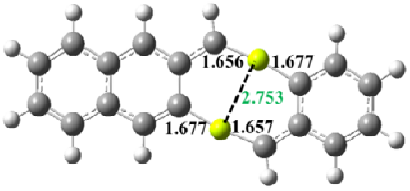
2Be-1A-BS



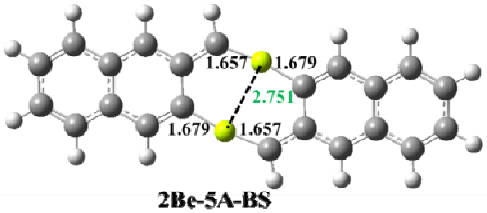
2Be-2A-BS



2Be-3A-BS



2Be-4A-BS



2Be-5A-BS

Figure S1. Optimized (UB3LYP/6-311++G**) geometries of multi-Be-expanded oligoacenes with indicated bond lengths (Å) and adjacent Be–Be distances (Å).

3. Optimized Molecular Geometries of Multi-Zn-Expanded Graphene Patches for Comparison

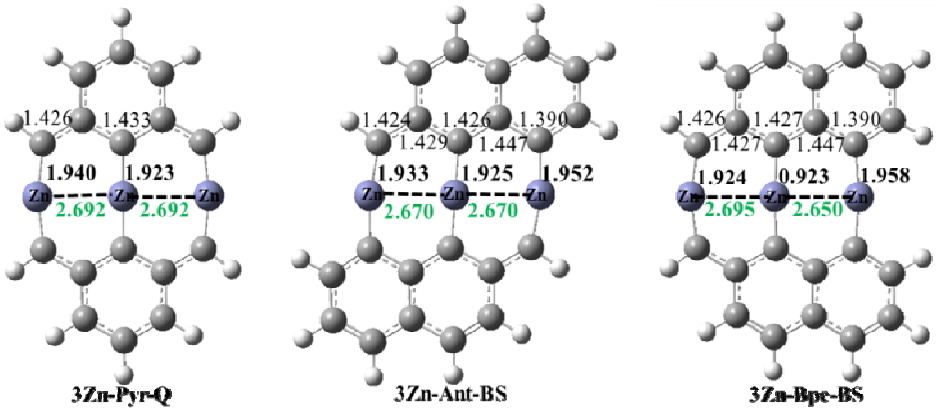


Figure S2. The optimized geometries of three multi-Zn-expanded graphene patches with indicated bond lengths (Å) and adjacent Zn-Zn distances (Å) at the UB3LYP/6-31G**(C,H)/SDD(Zn) level.

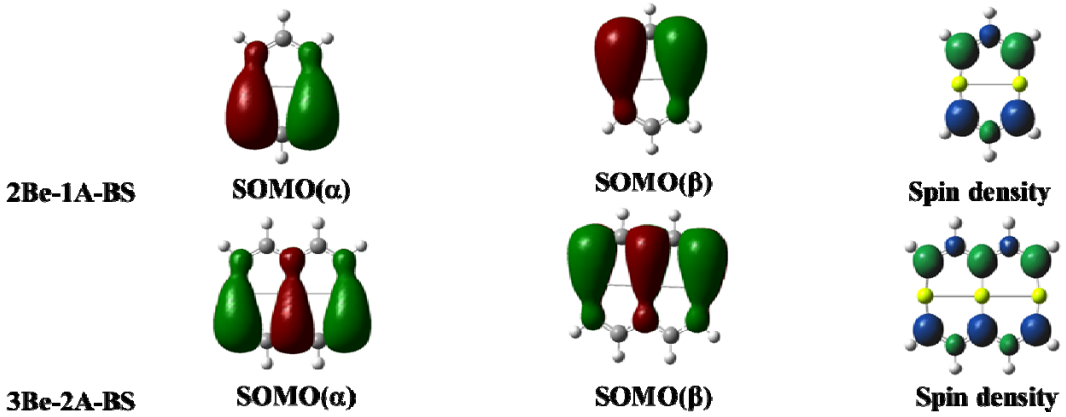
4. The J_{Be} and J_{Zn} Values for Be-Modified and Zn-Expanded Oligoacenes and Graphene Patches

Table S2. The *J* values of multi-Be-expanded oligoacenes and graphene patches as well as multi-Zn-expanded analogues.

(n+1)Be-nA	J_{Be} **(cm^{-1})**	J_{Zn} **(cm^{-1})**
2Be-1A	-1438.9	-930.4
3Be-2A	-1484.6	-888.1
2Be-nA	J_{Be} **(cm^{-1})**	J_{Zn} **(cm^{-1})**
2Be-1A	-1438.9	-930.4
2Be-2A	-1082.1	-670.3
2Be-3A	-540.9	-302.1
2Be-4A	-312.1	-173.6
2Be-5A	-149.5	-88.1
3Be-GP	J_{Be} **(cm^{-1})**	J_{Zn} **(cm^{-1})**
3Be-Ant	-503.6	-288.8
3Be-Bpe	-1250.6	-740.1

5. SOMO Plots and Spin Density Maps of All Ground States of Be-Expanded Oligoacenes

(n+1)Be-nA (n=1,2) series:



2Be-nA (n=1–5) series:

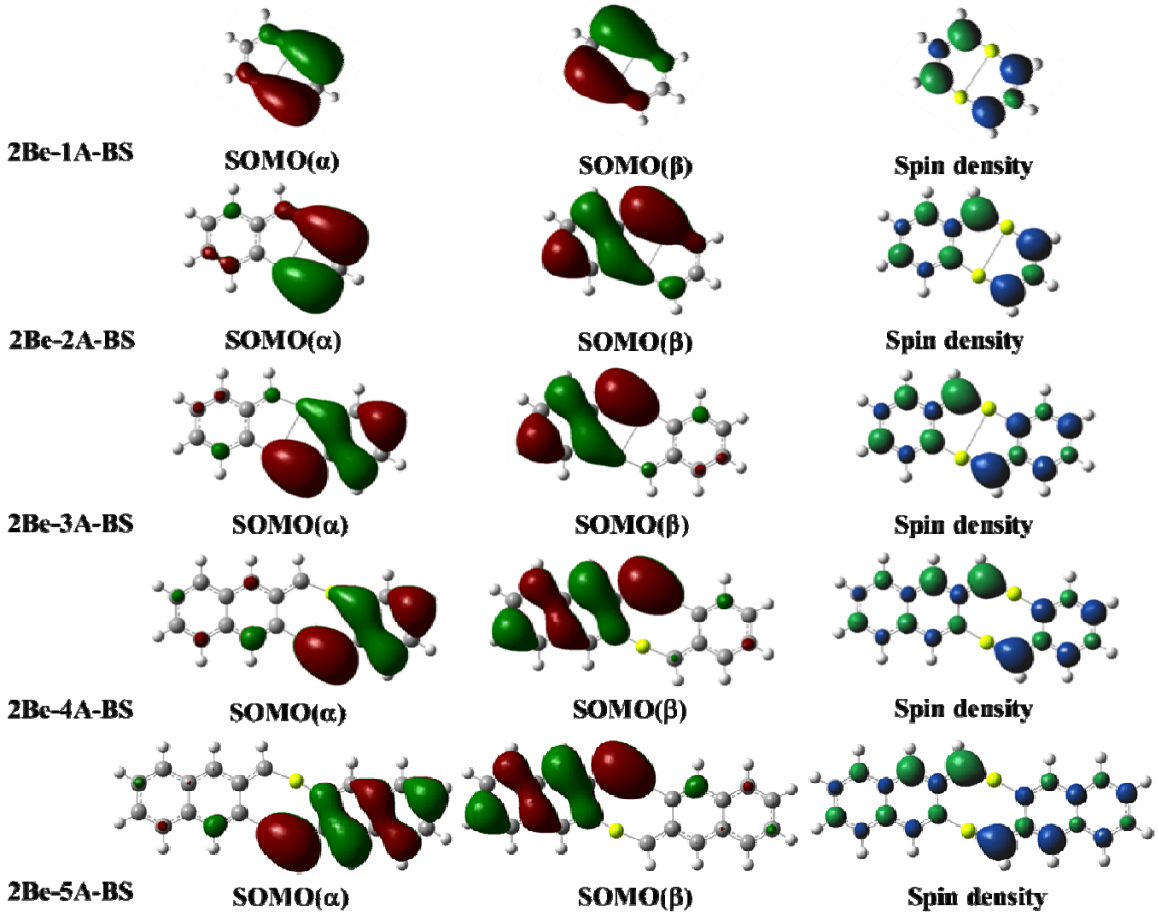


Figure S3. The singly occupied molecular orbitals (SOMO) of open-shell singlet multi-Be-expanded oligoacenes (isovalue = 0.02) and their corresponding spin density maps (isovalue = 0.004).

6. Relevant Data Calculated Using the CASSCF (10,10)/6-31G(d) Method

Table S3. The occupation numbers of LUMO and diradical percentages (%) calculated using the CASSCF(10,10)/6-31G(d) method.

(n+1)Be-nA	Occupation number of LUMO	Diradical Percentage %
2Be-1A	0.648	64.8
3Be-2A	0.563	56.3
2Be-nA	Occupation number of LUMO	Diradical Percentage %
2Be-1A	0.648	64.8
2Be-2A	0.697	69.7
2Be-3A	0.769	76.9
2Be-4A	0.837	83.7
2Be-5A	0.884	88.4
3Be-GP	Occupation number of LUMO	Diradical Percentage %
3Be-Ant	0.834	83.4
3Be-Bpe	0.612	61.2

7. Relevant Data of Energies for Singlet-Triplet Gaps and $<S^2>_{BS}$

Table S4. Energies (kcal/mol) for the singlet-triplet gaps ($\Delta E_{(T-BS)}$ or $\Delta E_{(T-CS)}$), and spin contamination for the open-shell singlet ($<S^2>$) of Be-expanded acenes and graphene patches and parent acenes calculated by Yang and co-workers.

(n+1)Be-nA	**$\Delta E_{(T-BS)}$**	**$<S^2>$**	**Acenes**	**$\Delta E_{(T-CS/BS)}$**	**$<S^2>$**
2Be-1A	5.13	0.80	1A	89.47	0.0
3Be-2A	5.71	0.73	2A	62.63	0.0
2Be-nA	**$\Delta E_{(T-BS)}$**	**$<S^2>$**	3A	41.80	0.0
2Be-1A	5.13	0.80	4A	27.75	0.0
2Be-2A	3.68	0.86	5A	17.94	0.0
2Be-3A	1.67	0.96	6A	10.89	0.0/0.25[a]
2Be-4A	0.92	1.01	7A	5.70/7.31[a]	0.0/0.80[a]
2Be-5A	0.43	1.05	8A	5.78	1.10
3Be-GP	**$\Delta E_{(T-BS)}$**	**$<S^2>$**	9A	5.33	1.25
3Be-Ant	1.55	0.97	10A	5.54	1.41
3Be-Bpe	4.57	0.78			

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

8. The HOMO-LUMO Gaps

Table S5. HOMO-LUMO Gaps (eV) for the closed-shell singlet states of parent acenes, multi-Be-expanded acenes, multi-Be-expanded graphene patches, and their corresponding multi-Zn-modified acenes and graphene patches.

(n+1)Be-nA	Gaps	(n+1)Zn-nA	Gaps	Acenes	Gaps
2Be-1A	1.79	2Zn-1A	2.94	1A	6.79
3Be-2A	1.64	3Zn-2A	2.44	2A	4.82
2Be-nA	**Gaps**	**2Zn-nA**	**Gaps**	**Acenes**	**Gaps**
2Be-1A	1.79	2Zn-1A	2.94	1A	6.79
2Be-2A	1.55	2Zn-2A	2.49	2A	4.82
2Be-3A	1.22	2Zn-3A	2.44	3A	3.59
2Be-4A	1.03	2Zn-4A	2.26	4A	2.78
2Be-5A	0.83	2Zn-5A	1.15	5A	2.21
3Be-GP	**Gaps**	**3Zn-GP**	**Gaps**	**GP**	**Gaps**
3Be-Ant	1.15	3Zn-Ant	0.94	Ant	2.87
3Be-Bpe	1.47	3Zn-Bpe	1.22	Bpe	3.48

9. SOMO Plots and Spin Density Maps and Coupling Modes of Be-Expanded Pyrene

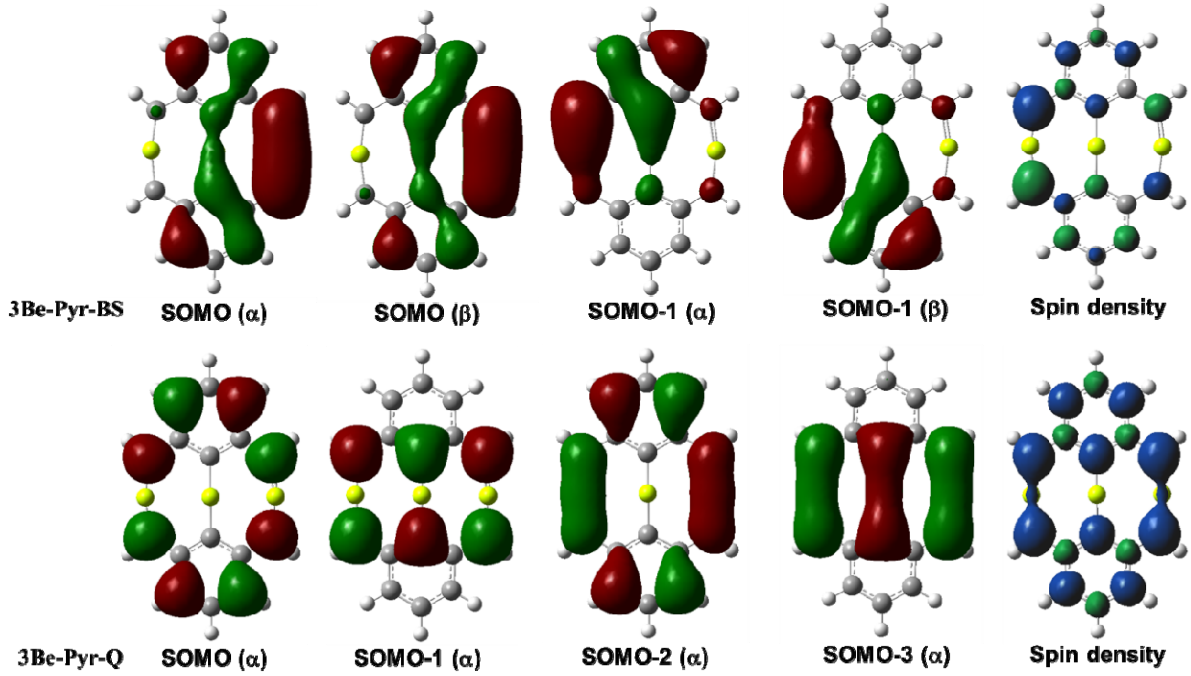


Figure S4. SOMOs (the left eight) and spin density map (the right two) of open-shell BS singlet and quintet ground state of 3Be-expanded pyrene (3Be-Pyr) which was performed at the UB3LYP/6-311++G** level (isovalue = 0.02 for orbitals and 0.004 for spin density map).

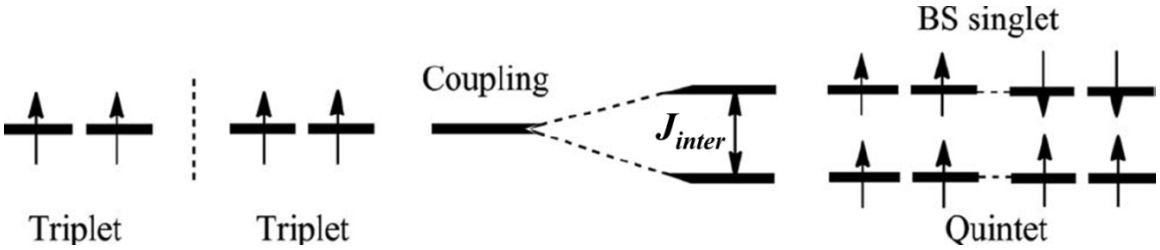


Figure S5. The most possible coupling modes of 3Be-expanded pyrene (3Be-Pyr).

10. Relevant Data of Adiabatic and Vertical Ionization Potentials and Adiabatic and Vertical Electron Affinities

Table S6. The adiabatic and vertical ionization potentials (AIP, VIP) of parent acenes and Be-doped acenes, the differences (ΔAIP^{Be}, ΔVIP^{Be}) between the Be-doped and parent acenes (in eV) calculated using B3LYP/6-311G**and the differences (ΔAIP^{Zn}, ΔVIP^{Zn}) between the Zn-doped and parent acenes (in eV) calculated using the B3LYP/C,H/6-311G**//Zn/SDD method.

Acenes	**AIP**	**VIP**	**IP^{exp}**		**AIP** (best theor est)	**VIP** (best theor est)	VIP^{theor} (OVGF)[a]
1A	9.09	9.24	9.24378±0.00007		9.22(4)	9.44(8)	9.044
2A	7.82	7.92	8.144±0.001		8.24(1)	8.24(1)	7.847
3A	7.04	7.11	7.439±0.006		7.41(9)	7.47(3)	7.202
4A	6.51	6.57	6.97±0.05		6.91(4)	6.94(8)	6.533
5A	6.13	6.18	6.63±0.05		6.55(6)	6.57(3)	6.150
(n+1)Be-nA	**AIP**	**VIP**	**ΔAIP^{Be}**	**ΔVIP^{Be}**	**ΔAIP^{Zn}**	**ΔVIP^{Zn}**	
2Be-1A	6.89	6.95	-2.20	-2.29	-2.70	-2.80	
3Be-2A	6.39	6.44	-1.43	-1.48	-1.91	-1.97	
2Be-nA	**AIP**	**VIP**	**ΔAIP^{Be}**	**ΔVIP^{Be}**	**ΔAIP^{Zn}**	**ΔVIP^{Zn}**	
2Be-1A	6.89	6.95	-2.20	-2.29	-2.70	-2.80	
2Be-2A	6.38	6.45	-1.44	-1.47	-1.87	-1.91	
2Be-3A	6.00	6.04	-1.04	-1.07	-1.39	-1.43	
2Be-4A	5.75	5.79	-0.76	-0.78	-1.06	-1.09	
2Be-5A	5.54	5.57	-0.59	-0.61	-0.85	-0.87	

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

Table S7. The adiabatic and vertical electron affinities (AEA, VEA) of parent acenes and Be-doped acenes, the differences (ΔAEA^{Be}, ΔVEA^{Be}) between the Be-doped and parent acenes (in eV) calculated using B3LYP/6-311G** and the differences (ΔAEA^{Zn}, ΔVEA^{Zn}) between the multi-Zn-expanded and parent acenes (in eV) calculated using the B3LYP/C,H/6-311G**//Zn/SDD method.

Acenes	**AEA**	**VEA**	**$EA^{(exp)}$**		**VEA(OVGF)[a]**	
1A	-1.68	-1.88	-1.12±0.03		-2.605	
2A	-0.42	-0.56	-0.19±0.03		-1.304	
3A	0.42	0.32	0.530±0.005		-0.438	
4A	1.00	0.92	1.04±0.04		+0.158	
5A	1.42	1.35	1.35±0.04		+0.585	
(n+1)Be-nA	**AEA**	**VEA**	**ΔAEA^{Be}**	**ΔVEA^{Be}**	**ΔAEA^{Zn}**	**ΔVEA^{Zn}**
2Be-1A	1.52	1.48	3.20	3.36	3.23	3.40
3Be-2A	1.71	1.67	2.13	2.23	2.15	2.26
2Be-nA	**AEA**	**VEA**	**ΔAEA^{Be}**	**ΔVEA^{Be}**	**ΔAEA^{Zn}**	**ΔVEA^{Zn}**
2Be-1A	1.52	1.48	3.20	3.36	3.23	3.40
2Be-2A	1.72	1.68	2.14	2.24	2.16	2.27
2Be-3A	1.95	1.90	1.53	1.58	1.53	1.59
2Be-4A	2.17	2.12	1.17	1.20	1.16	1.20
2Be-5A	2.35	2.29	0.93	0.94	0.90	0.94

Notes: The values of $EA^{(exp)}$ and VEA(OVGF) of parent acenes are from ref. Bendikov, M.; Dmitrii, F. W.; Perepichka, F. *Chem. Rev.* **2004**, *104*, 4891–4945. [a] At the OVGF/cc-pVDZ//B3LYP/cc-pVDZ level.

11. Topological Representation of Bond Dissociation Energies

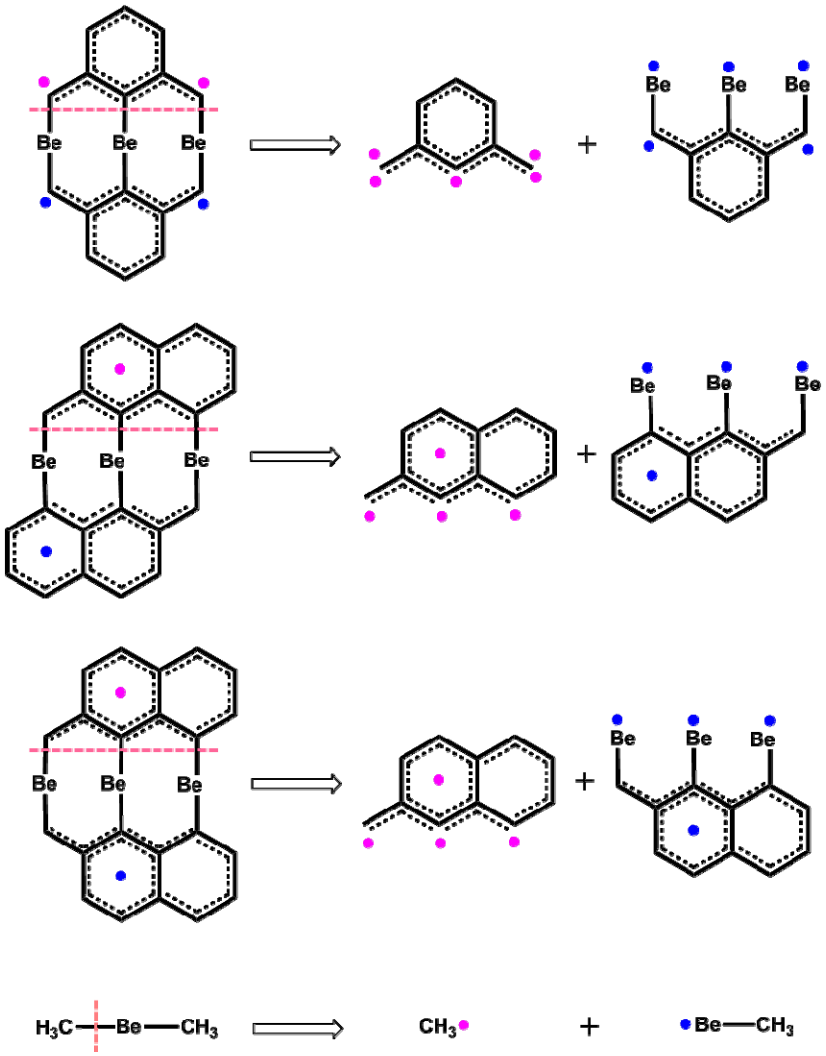


Figure S6. Topological representation of the bond dissociation energies of multi-Be expanded graphene patches and dimethylberyllium ($H_3C–Be–CH_3$). **Notes**: The calculation method of the dissociation energies is as shown above. The values are the energy differences between the Be-linked graphene patch and two corresponding semi-structures (two dissociated fragments), that is, the energies of the latter two semi-structures minus the energy of the former parent molecule. Providing that these multi-Be graphene patches are all polyradical molecules, and the corresponding two semi-structures are also polyradicals, as shown above. Different molecules may dissociate to different semi-structures with different polyradical characters, and we just take the above four molecules as examples for notation.