Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Spin Coupling Interactions in the C=C or B-B-Cored Porphyrin-Mimetic Graphene Patch Nitroxide Diradicals

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Supplementary Material

Contents

1. The Main Results for All Molecules

Table S1. Total Energies of the Closed-Shell Singlet (CS) Calculated at the B3LYP/6-311G(d, p) Level, Open-Shell BS Singlet and Triplet States Calculated at the UB3LYP/6-311G(d, p) Level, Corresponding $<S^2>$ Values, Singlet-Triplet Energy Gaps ($\Delta E_{(BS-T)}$, kcal/mol) and Intramolecular Magnetic Coupling Constants (J, in cm^{-1}) of Diradicals.

CC-cored Molecules	**$E_{(CS)}$**	**$E_{(BS)}$ ($<S^2>$)**	**$E_{(T)}$ ($<S^2>$)**	**$\Delta E_{(BS-T)}$**	***J***
CC-m_1m_1	-1336.6654379	-1336.686568 (1.017)	-1336.6861499 (2.017)	-0.262	-91.8
CC-$\beta_1\beta_1$	-1336.719923	-1336.7209720 (0.646)	-1336.7109195 (2.027)	-6.308	-1597.3
CC-$\beta_2\beta_2$	-1336.6814231	-1336.7024236 (1.041)	-1336.7011792 (2.037)	-0.781	-274.2
CC-m_2m_2	-1336.6654379	-1336.6697525 (1.011)	-1336.6697386 (2.009)	-0.009	-3.1
CC-$m_1\beta_1$	-1336.6920567	-1336.7021121 (1.001)	-1336.6997537 (2.074)	-1.480	-482.4
CC-$\beta_1\beta_2$	-1336.6959155	-1340.1330408 (1.053)	-1340.1344268 (2.098)	0.777	257.2
CC-$m_1\beta_2$	-1336.6780184	-1336.6937394 (1.030)	-1336.6942444 (2.040)	0.317	109.7
CC-m_1m_2	-1336.6464977	-1340.101063 (1.012)	-1340.1011612 (2.013)	0.100	34.7
CC-$m_2\beta_1$	-1336.6622065	-1336.6924072 (1.073)	-1336.6929825 (2.092)	0.361	123.9
CC-$m_2\beta_2$	-1336.6748068	-1336.6861984 (1.026)	-1336.6855593 (2.026)	-0.401	-140.3
BB-cored Molecules	**$E_{(CS)}$**	**$E_{(BS)}$ ($<S^2>$)**	**$E_{(T)}$ ($<S^2>$)**	**$\Delta E_{(BS-T)}$**	***J***
BB-m_1m_1	-1310.1202084	-1310.1313314 (1.199)	-1310.1369909 (2.344)	3.551	1084.8
BB-m_2m_2	-1310.0933821	-1310.1066924 (1.375)	-1310.1081064 (2.472)	0.887	282.9
BB-m_1m_2	-1310.1030042	-1310.1193275 (1.194)	-1310.1207493 (2.334)	0.892	273.7

Table S2. Energies and $<S^2>$ values for the triplet state and two excited states of four representative molecules calculated by the spin-flip-PBE50/6-311G(d,p) and spin-flip-5050/6-311G(d,p) methods using non-collinear kernels.

	Molecules	**SCF energies of Ref Triplet State ($<S^2>$)**	**Excited state 1 ($<S^2>$)**	**Excited state 2 ($<S^2>$)**
SF-PBE50	**CC-m_1m_1**	-1335.25464590 (2.1561)	-1335.24273552 (0.1932)	-1335.24251742 (2.2133)
	CC-$\beta_1\beta_1$	-1335.27616231 (2.0655)	-1335.27373437 (0.4907)	-1335.24420052 (1.1779)
	CC-$m_1\beta_1$	-1335.27027392 (2. 4818)	-1335.25926135 (1.3478)	-1335.24717638 (2.1267)
	CC-$\beta_1\beta_2$	-1335.27984138 (2.5758)	-1335.26079061 (2.1143)	-1335.25395868 (1.7800)
	Molecules	**SCF energies of Ref Triplet State ($<S^2>$)**	**Excited state 1 ($<S^2>$)**	**Excited state 2 ($<S^2>$)**
SF-5050	**CC-m_1m_1**	-1335.70102058 (2.0912)	-1335.68550444 (0.1347)	-1335.68524426 (2.1392)
	CC-$\beta_1\beta_1$	-1335.72357995 (2.0608)	-1335.71864166 (0.5235)	-1335.68932654 (1.1405)
	CC-$m_1\beta_1$	-1335.71649080 (2.4182)	-1335.70176455 (1.2311)	-1335.69163723 (2.1331)
	CC-$\beta_1\beta_2$	-1335.72603550 (2.5146)	-1335.70438472 (2.0671)	-1335.69839818 (1.6938)

2. Comparison Between the Porphyrin-Mimetic Graphene Patch Coupler and Common Graphene Patch Coupler

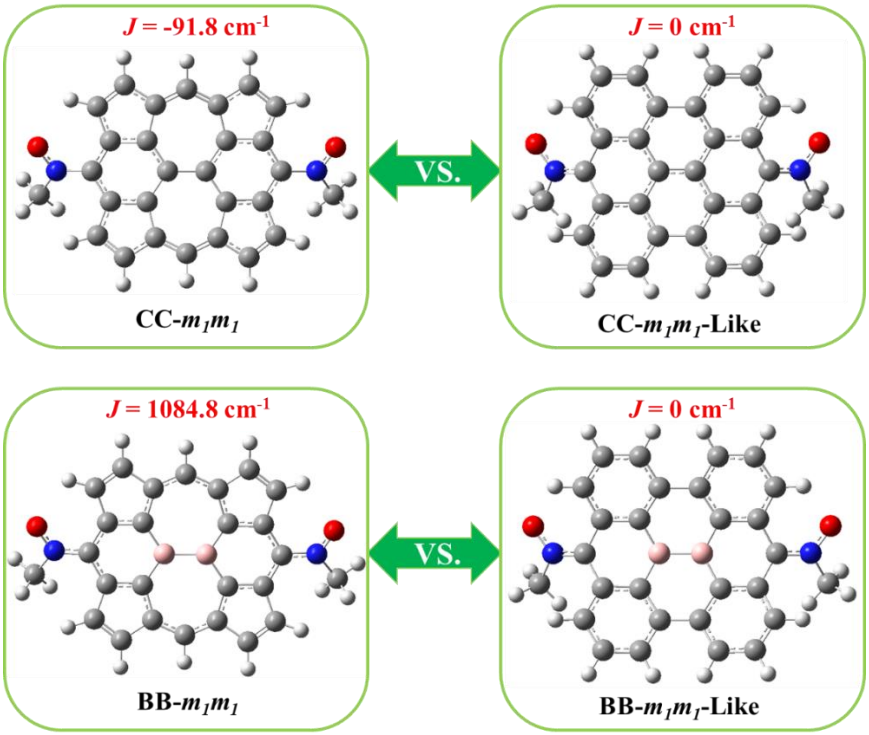
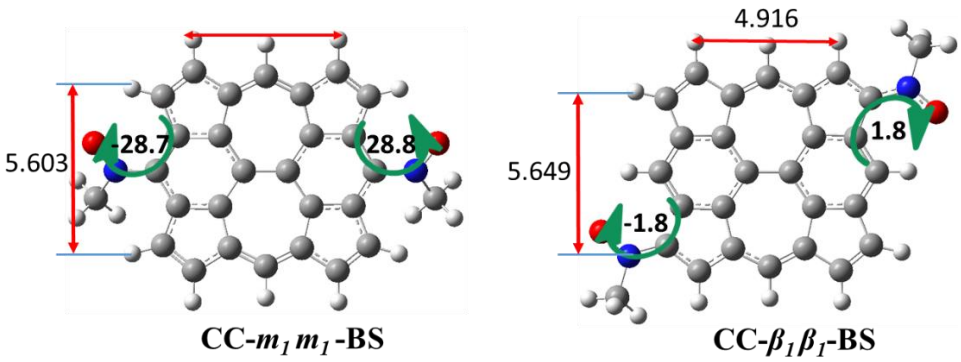
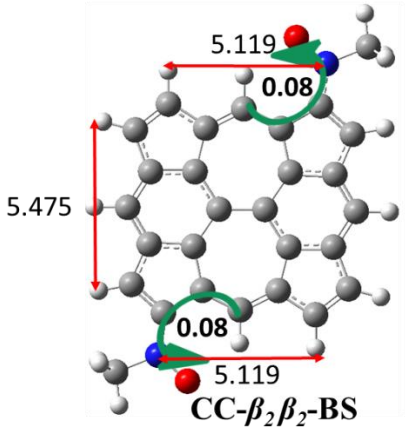


Figure S1. Comparison of magnetic interactions between CC-m_1m_1 and CC-m_1m_1-like as well as BB-m_1m_1 and BB-m_1m_1-like.

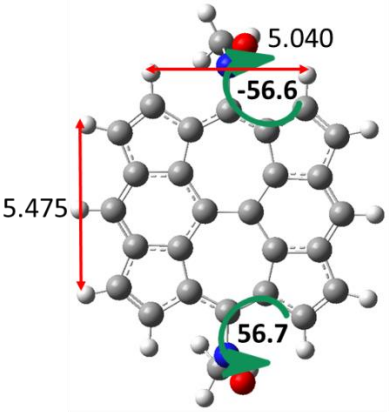
3. All Optimized Diradical Molecular Geometries and Structural Effects

The CC-Cored Molecules:

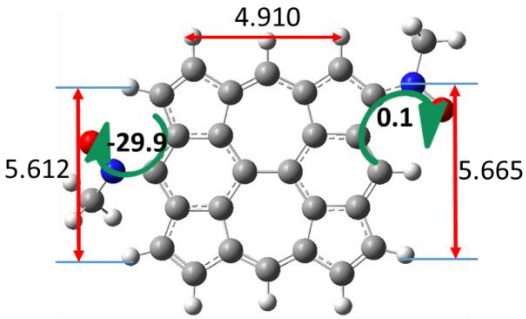




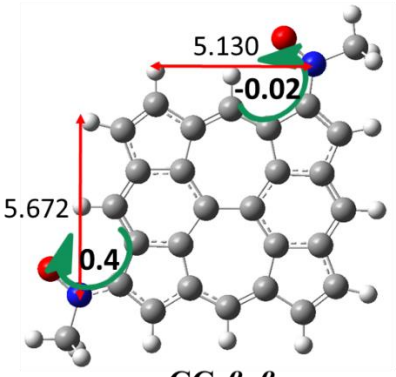
CC-$\beta_2\beta_2$-BS



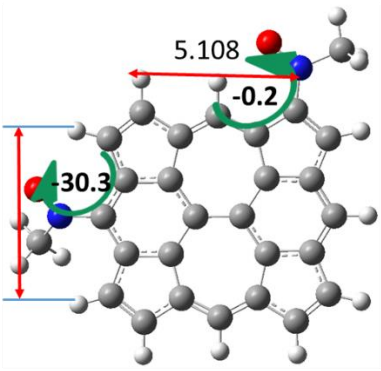
CC-m_2m_2-BS



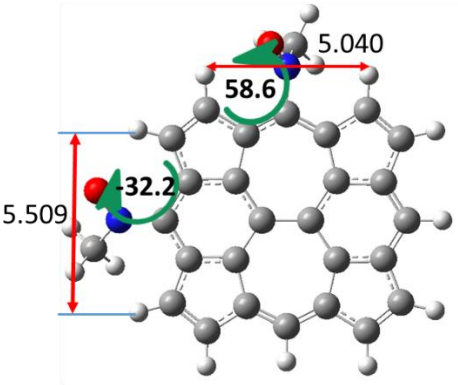
CC-$m_1\beta_1$



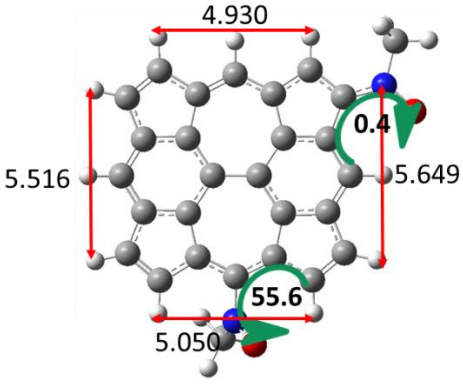
CC-$\beta_1\beta_2$



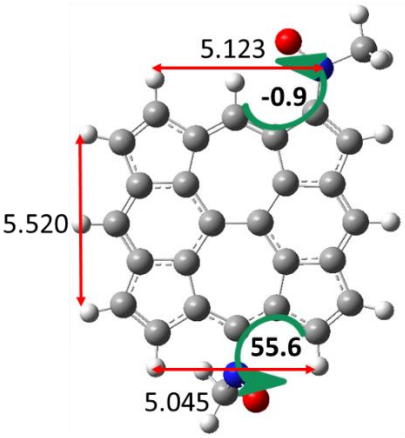
CC-$m_1\beta_2$



CC-m_1m_2



CC-$m_2\beta_1$



CC-$m_2\beta_2$

The BB-Cored Molecules:

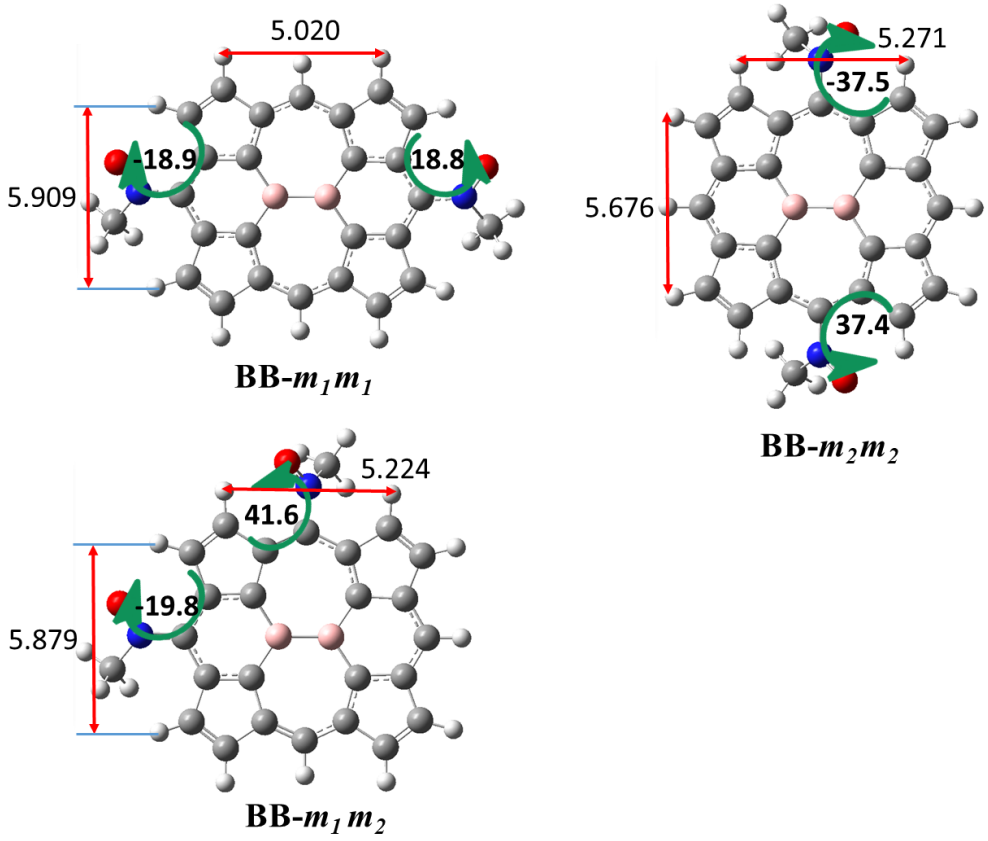


Figure S2. The optimized molecular geometries with dihedral angles about the diradical molecules in more stable spin states calculated at the UB3LYP/6-311G (d,p) level. The molecule marked by a suffix BS denotes that its ground state is the BS state, while others have the triplet ground states.

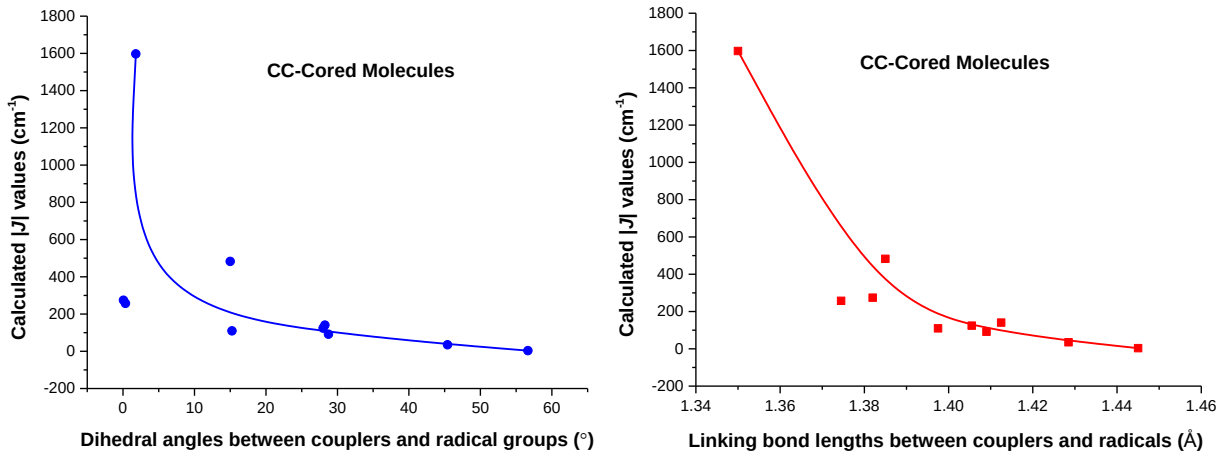
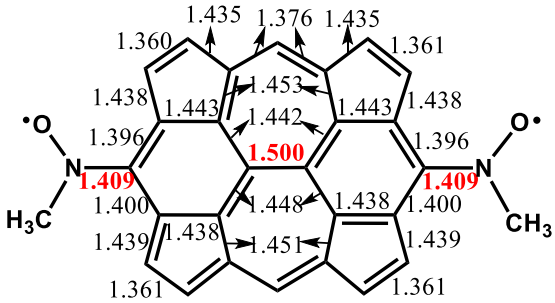
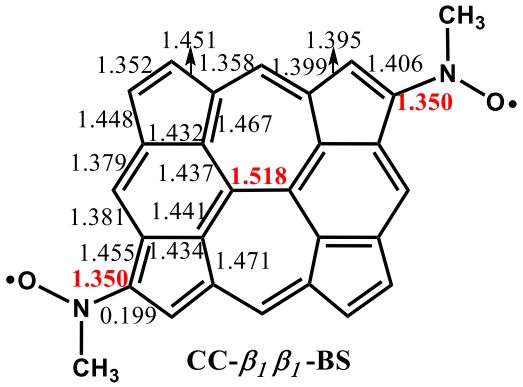


Figure S3. Structural effects including average dihedral angles and linking bond length between the coupler and nitroxide radical group.

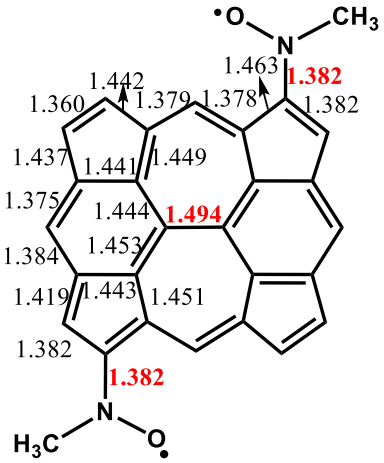
The CC-Cored Molecules:



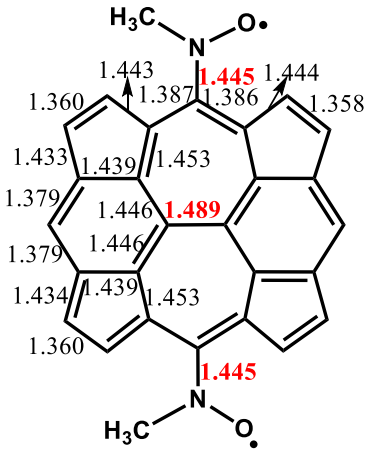
CC-$m_1 m_1$-BS



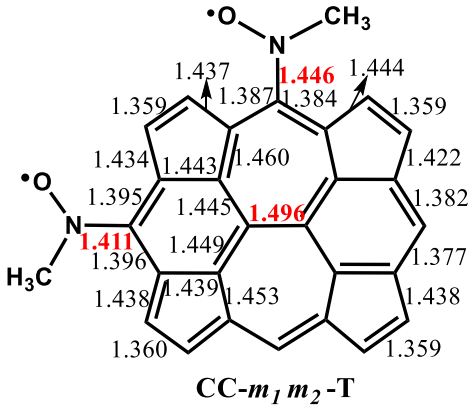
CC-$\beta_1 \beta_1$-BS



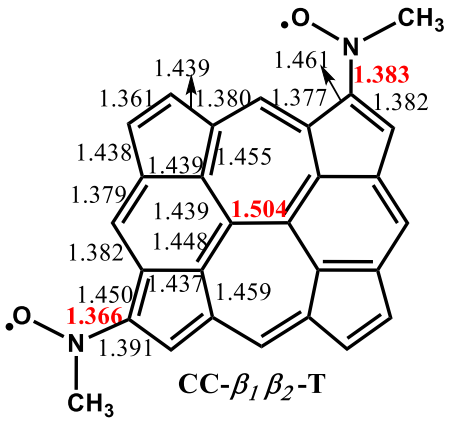
CC-$\beta_2 \beta_2$-BS



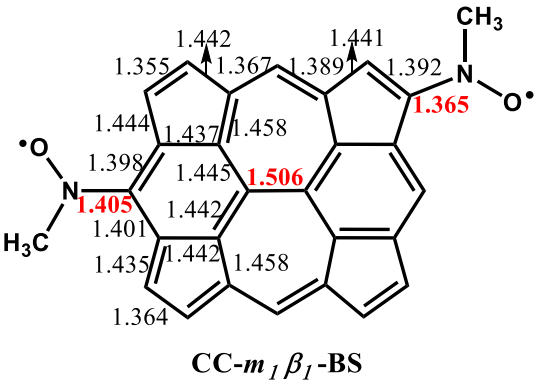
CC-$m_2 m_2$-BS



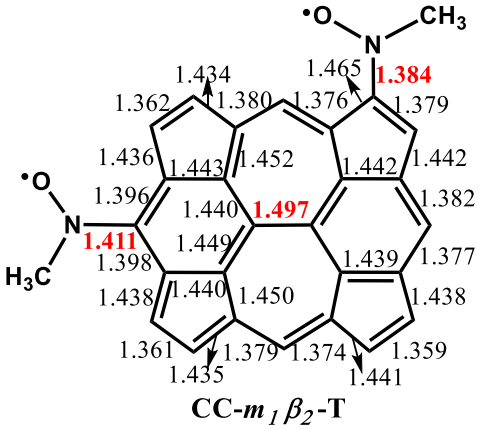
CC-$m_1 m_2$-T



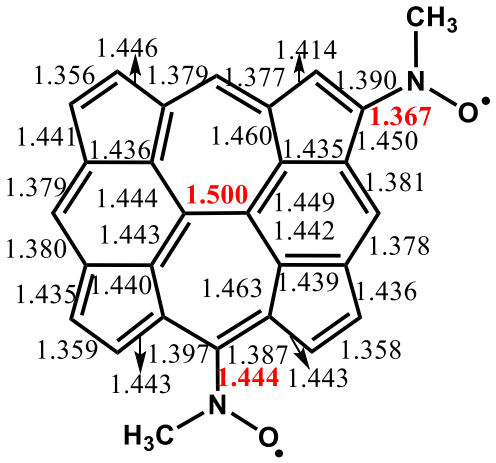
CC-$\beta_1 \beta_2$-T



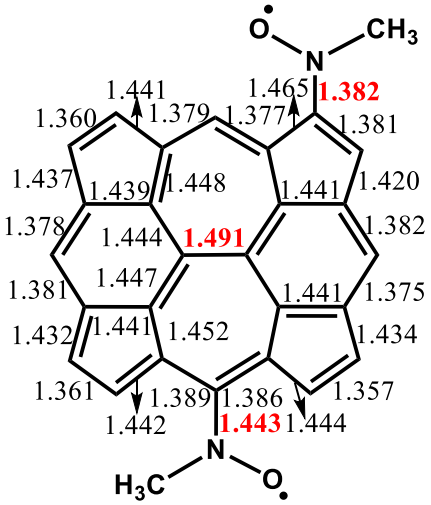
CC-$m_1 \beta_1$-BS



CC-$m_1 \beta_2$-T

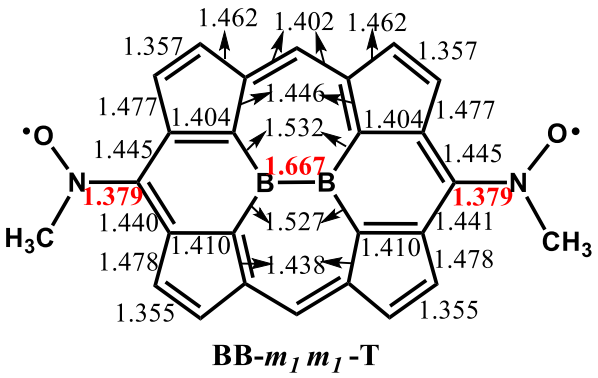


CC-$m_2\beta_1$-T

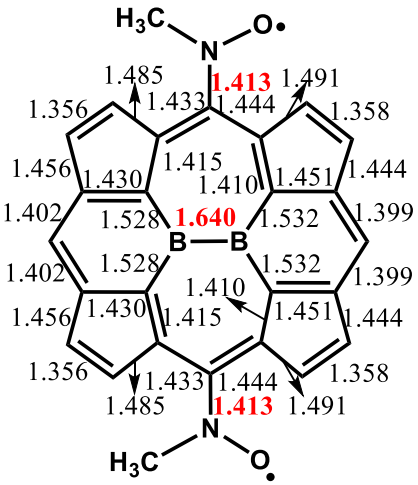


CC-$m_2\beta_2$-BS

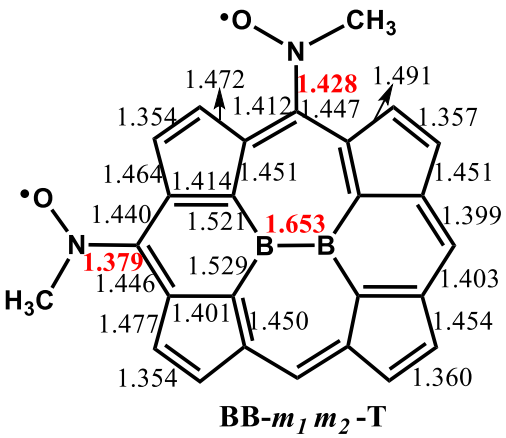
The BB-Cored Molecules:



BB-m_1m_1-T



BB-m_2m_2-T



BB-m_1m_2-T

Figure S4. The bond lengths (Å) of optimized geometries at the UB3LYP/6-311G (d,p) level. The suffix BS denotes the BS ground state, while T denotes the triplet ground state.

4. Structural Effects on the *J* Values

Table S3. |*J*| Values (cm^{-1}), Average Dihedral Angles (°) and Linking Bond Lengths (Å) Between the Coupler and the Nitroxide Radical Group.

CC-Cored Molecules	|*J*|	Average dihedral angel	CC-Cored Molecules	|*J*|	Linking bond length
CC-$\beta_2\beta_2$	274.2	0.08	CC-$\beta_1\beta_1$	1597.3	1.350
CC-$\beta_1\beta_2$	257.2	0.35	CC-$\beta_1\beta_2$	257.2	1.375
CC-$\beta_1\beta_1$	1597.3	1.80	CC-$\beta_2\beta_2$	274.2	1.382
CC-$m_1\beta_1$	482.4	15.00	CC-$m_1\beta_1$	482.4	1.385
CC-$m_1\beta_2$	109.7	15.25	CC-$m_1\beta_2$	109.7	1.398
CC-$m_2\beta_1$	123.9	28.00	CC-$m_2\beta_1$	123.9	1.406
CC-$m_2\beta_2$	140.3	28.25	CC-m_1m_1	91.8	1.409
CC-m_1m_1	91.8	28.75	CC-$m_2\beta_2$	140.3	1.413
CC-m_1m_2	34.7	45.40	CC-m_1m_2	34.7	1.429
CC-m_2m_2	3.1	56.65	CC-m_2m_2	3.1	1.445
BB-Cored Molecules	**|*J*|**	**Average dihedral angel**	**BB-Cored Molecules**	**|*J*|**	**Linking bond length**
BB-m_1m_1	1084.8	18.85	BB-m_1m_1	1084.8	1.379
BB-m_1m_2	273.7	30.70	BB-m_1m_2	273.7	1.404
BB-m_2m_2	282.9	37.45	BB-m_2m_2	282.9	1.413

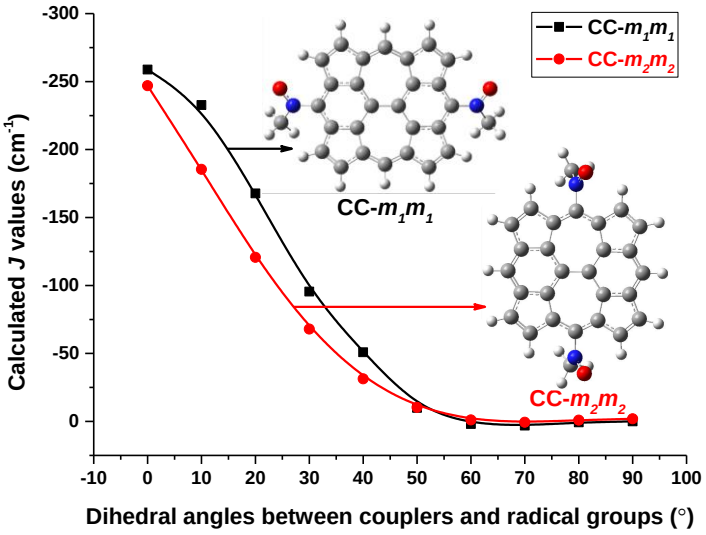


Figure S5. Relationship between the *J* values and dihedral angles between the coupler and radical groups in CC-m_1m_1 and CC-m_2m_2.

Table S4. Calculated Intramolecular Magnetic Coupling Constants (J, in cm^{-1}) of CC-m_1m_1 and CC-m_2m_2 Depending on the Dihedral Angles (0 ~ 90°).

Dihedral Angles (°)	J_{m1m1}	J_{m2m2}
0	-258.8	-247.0
10	-232.7	-185.4
20	-167.7	-120.7
30	-95.5	-67.9
40	-50.9	-31.3
50	-10.0	-10.3
60	1.9	-1.1
70	3.1	0.6
80	0.7	-0.9
90	0	-1.9

5. Schematic Diagram of Exchange Coupling between Two Radical Groups through the Coupler LUMO

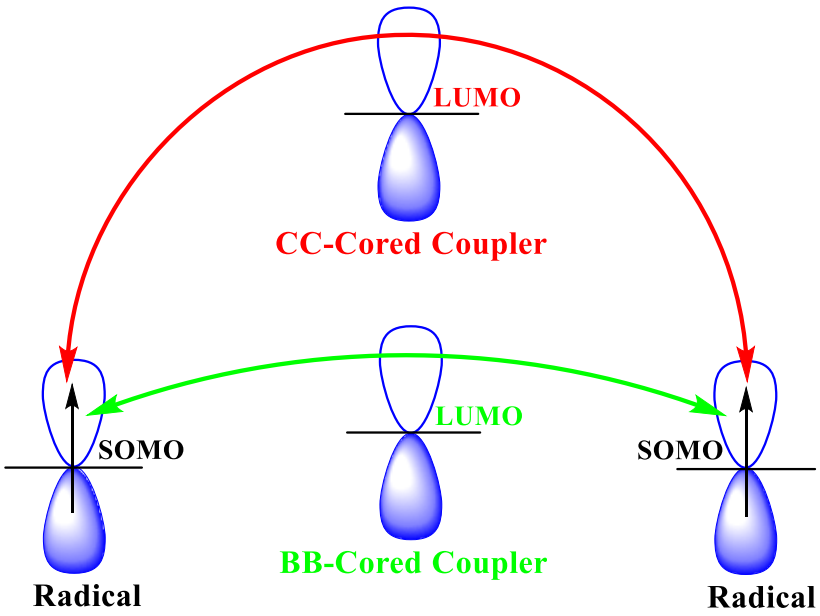


Figure S6. The schematic diagram of exchange coupling between two radical groups through LUMO of the different coupler. Location of the molecular orbitals (SOMOs and LUMO) roughly represent the high- or low-level in energy.

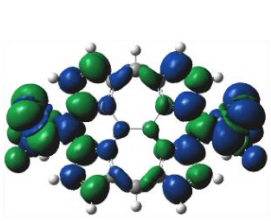
6. The HOMO-LUMO Gaps ($\Delta E_{H\text{-}L}$, kcal/mol) of the CS States

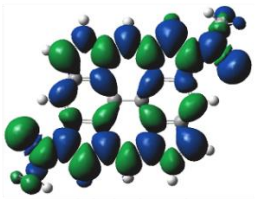
Table S5. HOMO-LUMO Gaps ($\Delta E_{H\text{-}L}$, kcal/mol) of CS States of All Molecules. BB-Cored Molecules Related to β_1- and β_2-Sites Have CS Ground States.

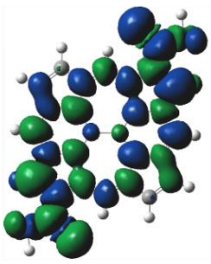
Molecules	$\Delta E_{H\text{-}L}$	J (cm^{-1})	Molecules	$\Delta E_{H\text{-}L}$	J (cm^{-1})
CC-m_1m_1	24.17	-91.8	BB-m_1m_1	15.54	1084.8
CC-$\beta_1\beta_1$	41.32	-1597.3	BB-$\beta_1\beta_1$	31.16	
CC-$\beta_1\beta_2$	23.12	257.2	BB-$\beta_1\beta_2$	35.39	
CC-$m_1\beta_1$	29.60	-482.4	BB-$m_1\beta_1$	37.90	CS
CC-$\beta_2\beta_2$	22.89	-274.2	BB-$\beta_2\beta_2$	44.62	
CC-$m_1\beta_2$	20.45	109.7	BB-$m_1\beta_2$	39.12	
CC-m_2m_2	23.32	-3.1	BB-m_2m_2	19.13	282.9
CC-m_1m_2	22.65	34.7	BB-m_1m_2	17.31	273.7
CC-$m_2\beta_2$	31.54	-140.3	BB-$m_2\beta_2$	35.55	CS
CC-$m_2\beta_1$	20.78	123.9	BB-$m_2\beta_1$	37.79	

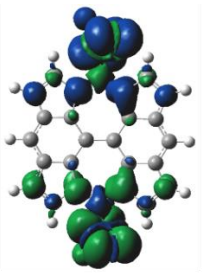
7. Spin Density Distributions

The CC-Cored Molecules:


CC-m_1 m_1 -BS


CC-β_1 β_1 -BS


CC-β_2 β_2 -BS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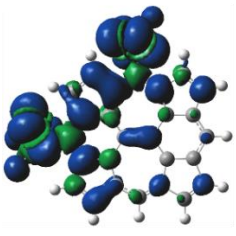
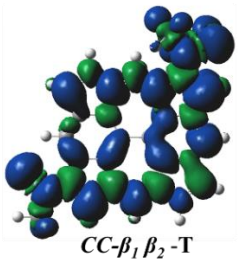
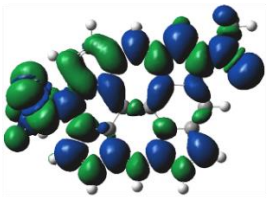
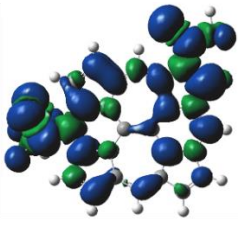
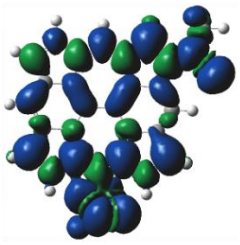
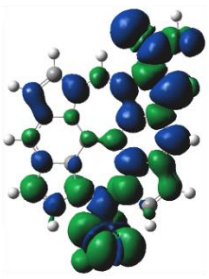

CC-m_1 m_2 -T


CC-β_1 β_2 -T


CC-$m_1\beta_1$-BS


CC-$m_1\beta_2$-T


CC-$m_2\beta_1$-T


CC-$m_2\beta_2$-BS

The BB-Cored Molecules:

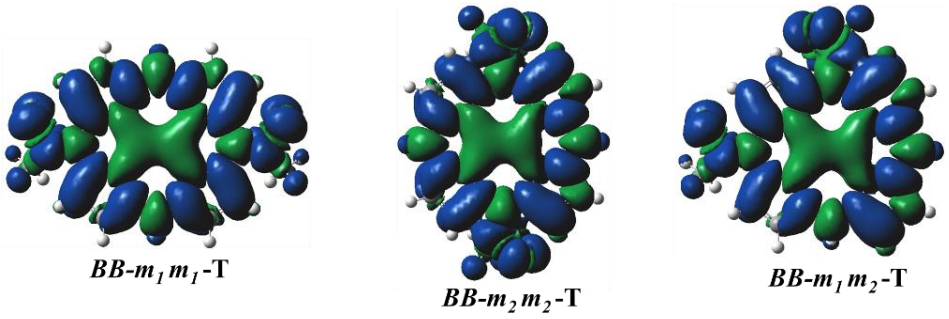
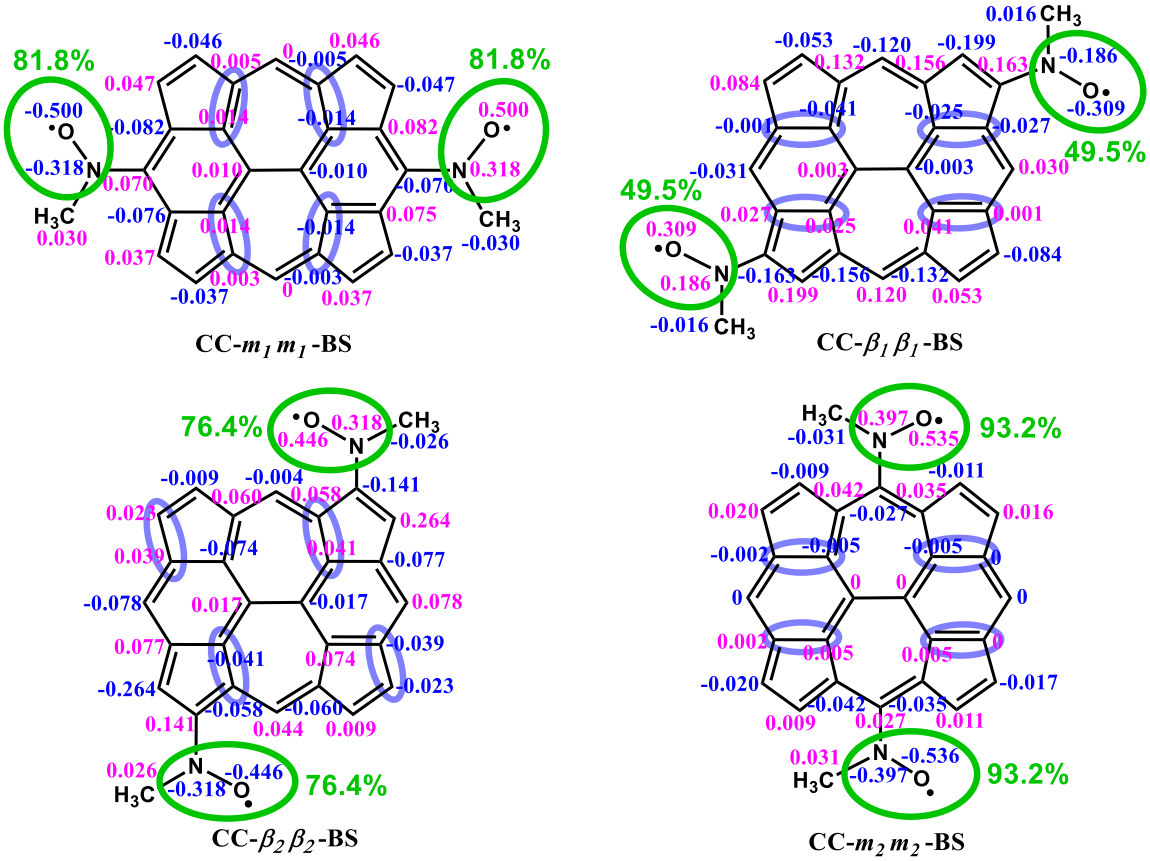
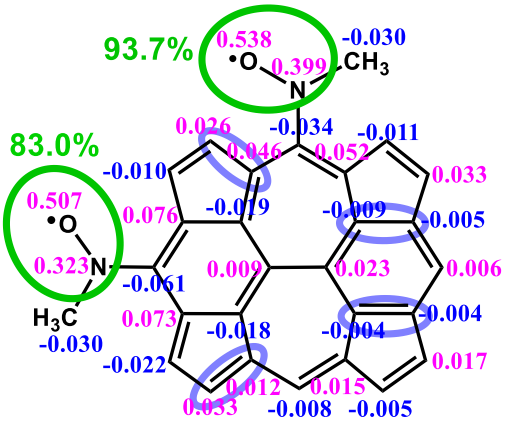


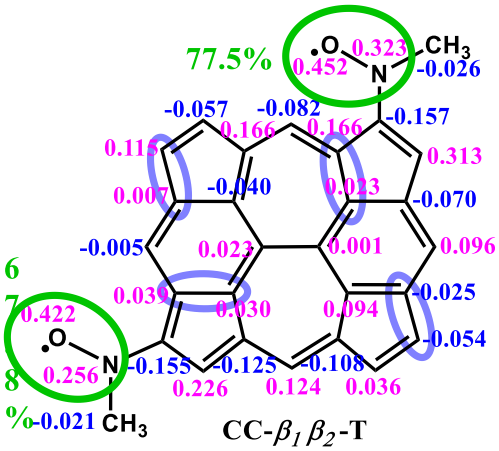
Figure S7. Spin density maps (isovalue = 0.0004) of the ground states of all BB-cored diradicals. The blue and green colors represent the α- and β-spins, respectively.

The CC-Cored Molecules:

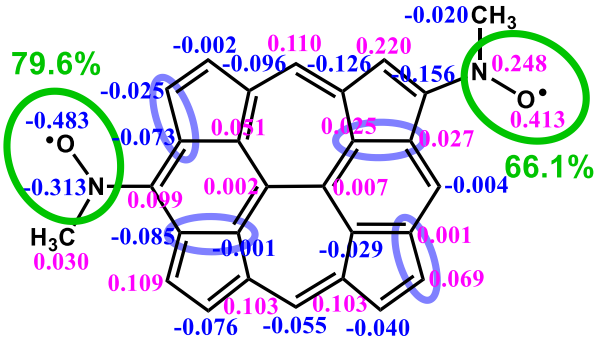




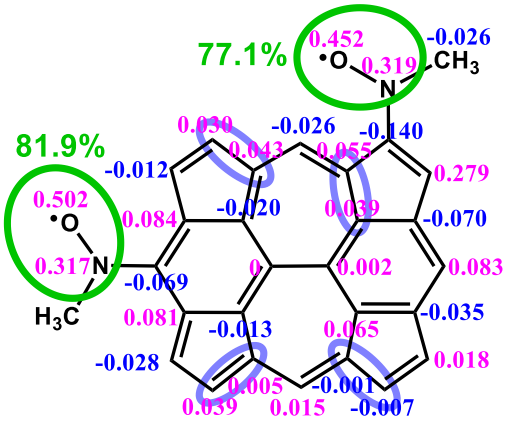
CC-$m_1 m_2$-T



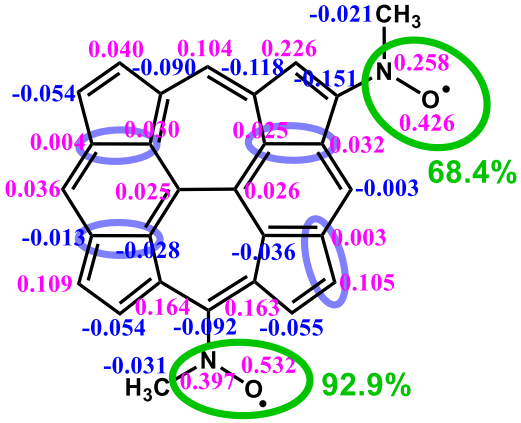
CC-$\beta_1 \beta_2$-T



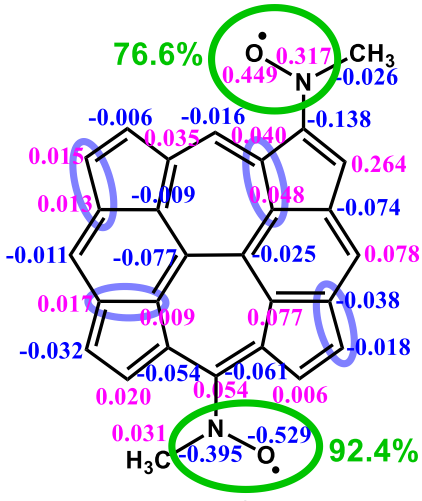
CC-$m_1 \beta_1$-BS



CC-$m_1 \beta_2$-T



CC-$m_2 \beta_1$-T



CC-$m_2 \beta_2$-BS

The BB-Cored Molecules:

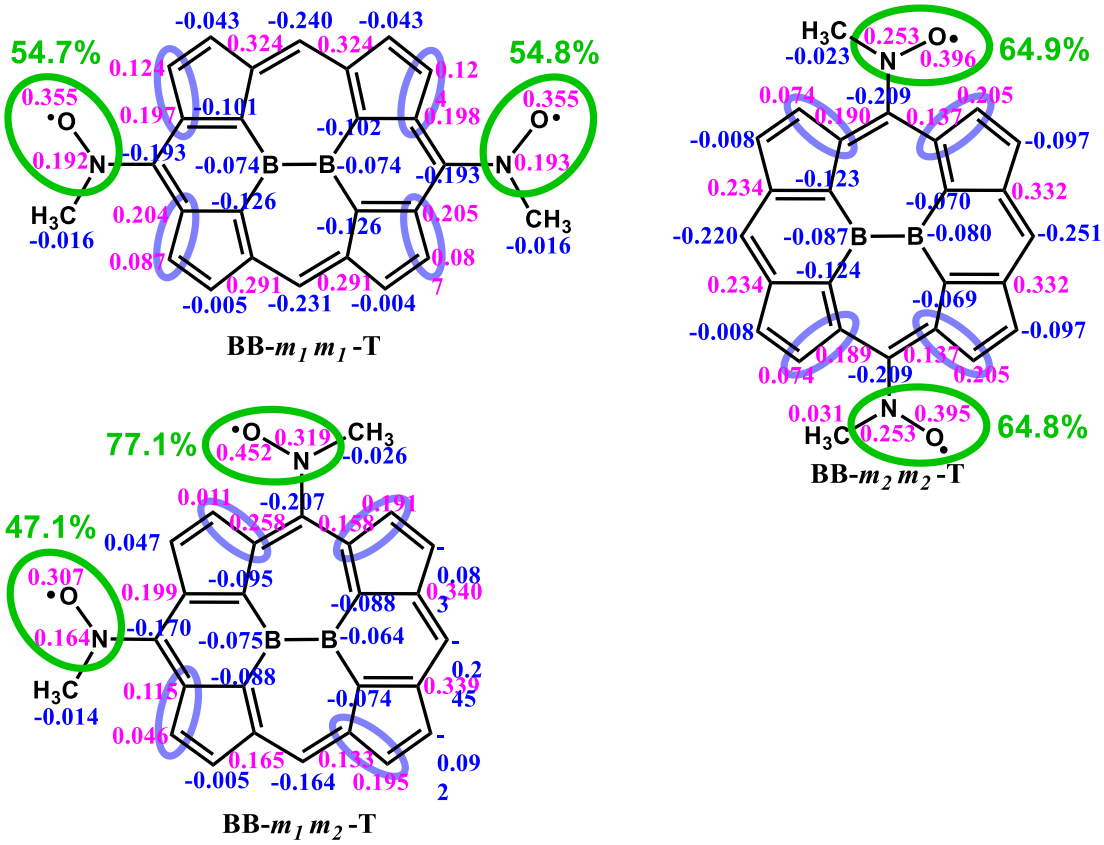
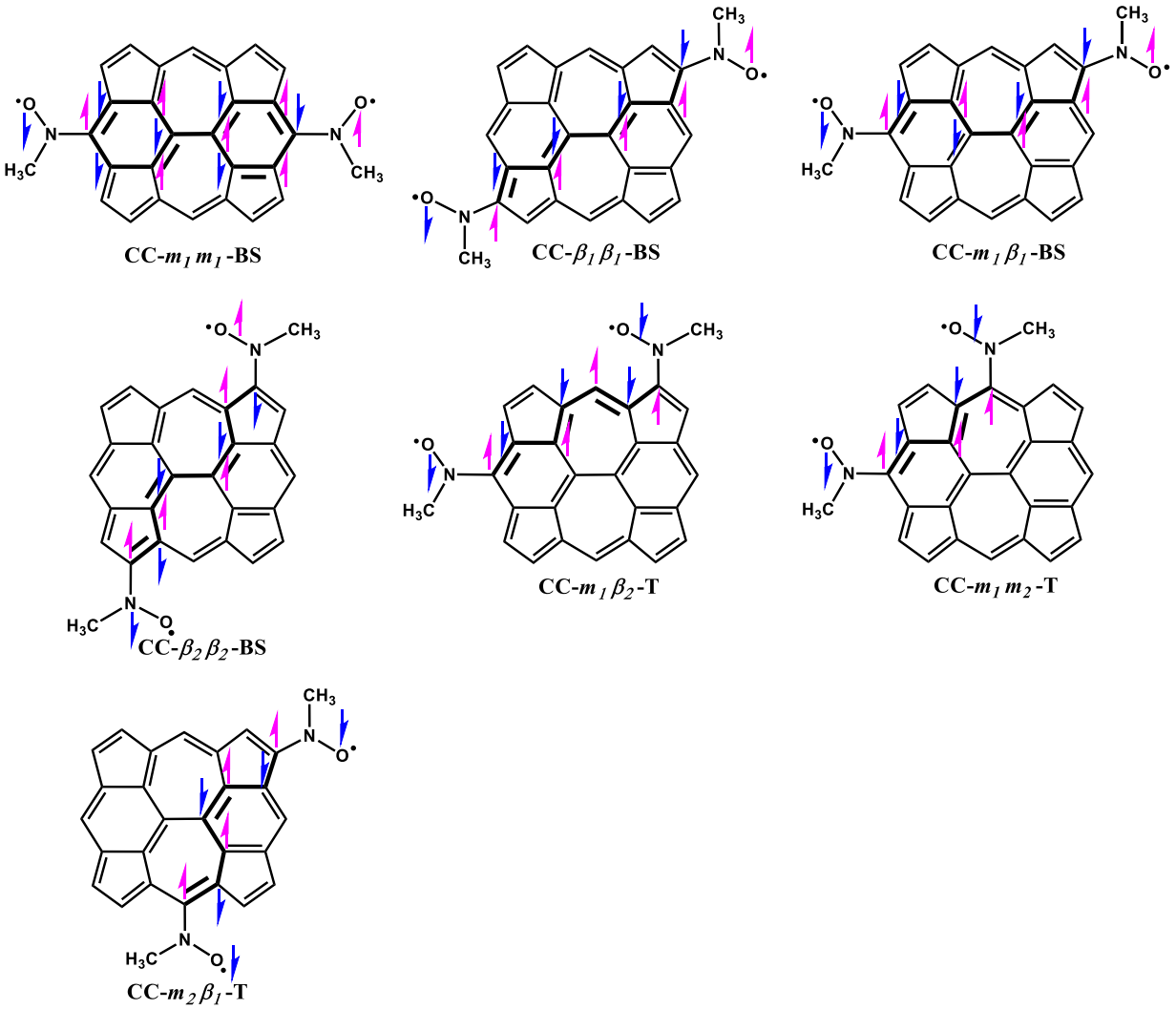


Figure S8. Spin density distributions. The pink and blue numbers denote α and β phase, respectively. The green circles and number denote the percentage of atomic spin density distributions of the NO radical, while purple circles denote the same phase of two adjacent atoms in the five-membered rings.

The CC-Cored Molecules:



The BB-Cored Molecules:

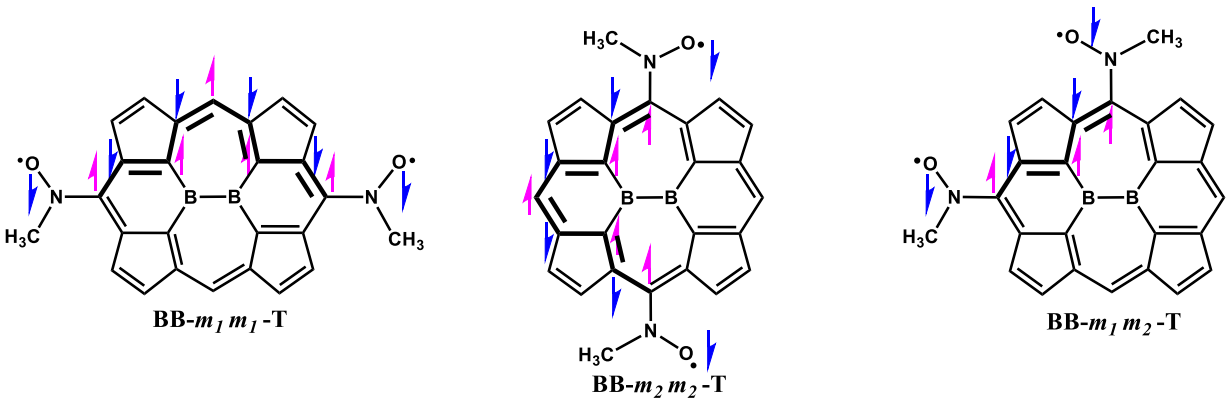


Figure S9. Spin alternation rule via the minimum path of the coupler.

Table S6. Calculated |*J*| Values and Average Percentages of Atomic Spin Density Distributions for the Diradical Delocalized over the Coupler in Each Diradical Molecule.

Molecules	|*J*|	Average Spin density (%)	Molecules	|*J*|	Average Spin density (%)
CC-m_1m_1	91.8	18.2	BB-m_1m_1	1084.8	45.3
CC-$\beta_1\beta_1$	1597.3	50.5	BB-m_2m_2	282.9	35.2
CC-$\beta_1\beta_2$	257.2	27.4	BB-m_1m_2	273.7	37.8
CC-$m_1\beta_1$	482.4	27.2			
CC-$\beta_2\beta_2$	274.2	23.6			
CC-$m_1\beta_2$	109.7	20.5			
CC-m_2m_2	3.1	6.8			
CC-m_1m_2	34.7	11.7			
CC-$m_2\beta_2$	140.3	15.5			
CC-$m_2\beta_1$	123.9	19.4			

8. Figures and Data of Molecular Vibration for the CC-Cored Molecules

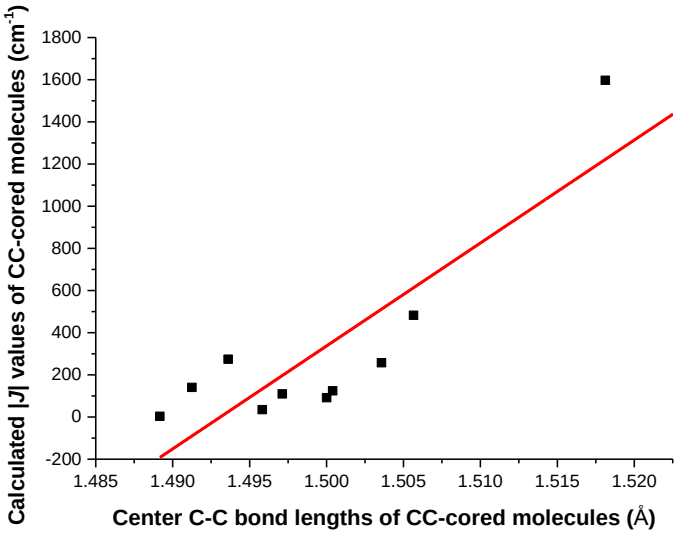
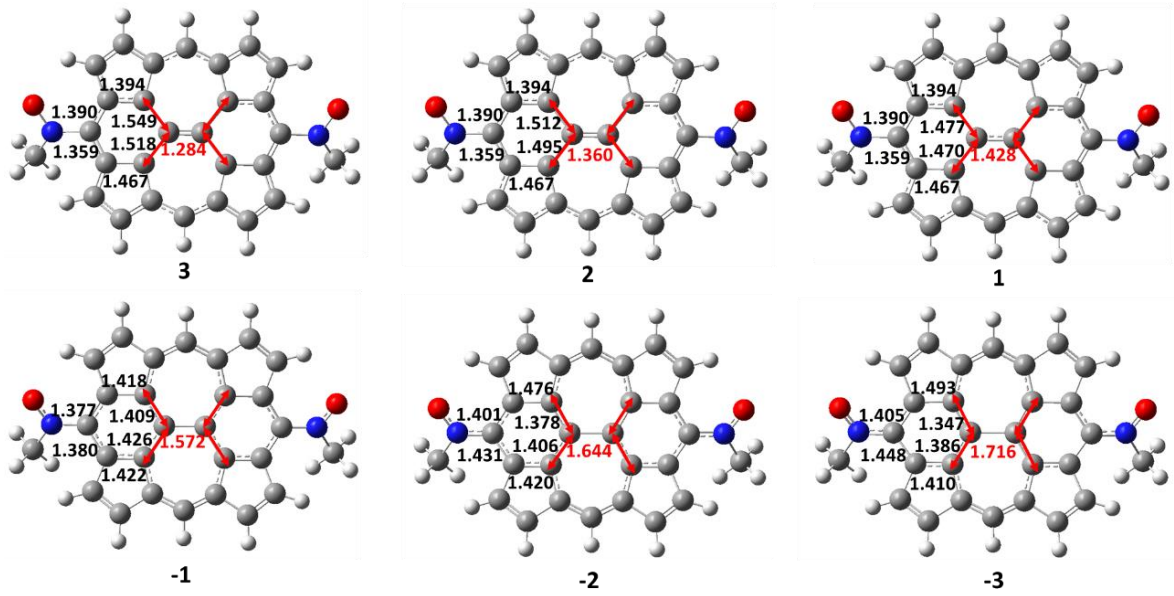


Figure S10. Relationship between the |*J*| values and center C-C bond lengths in the CC-cored molecules.

Table S7. Data about Average Dihedral Angles (°) and Center C-C Bond Lengths (Å) and Calculated *J* Values (cm^{-1}) of Relevant Snapshot Configurations for the CC-m_1m_1 and CC-$\beta_1\beta_1$ Molecules (n = -3~3).

CC-m_1m_1				CC-$\beta_1\beta_1$			
n	**Center C-C bond length**	**Average dihedral angel**	***J***	**n**	**Center C-C bond length**	**Average dihedral angel**	***J***
3.0	1.284	29.30	-9.5	3.0	1.373	1.95	-2047.2
2.5	1.320	29.22	-18.1	2.5	1.397	1.92	-2112.6
2.0	1.356	29.13	-29.1	2.0	1.422	1.89	-2175.8
1.5	1.392	29.04	-42.7	1.5	1.446	1.86	-2237.1
1.0	1.428	28.95	-59.4	1.0	1.470	1.83	-2296.8
0.5	1.464	28.85	-79.7	0.5	1.494	1.81	-2357.2
0.0	1.500	28.75	-103.9	0.0	1.518	1.79	-2413.9
-0.5	1.536	28.64	-132.6	-0.5	1.542	1.765	-2467.8
-1.0	1.572	28.53	-165.7	-1.0	1.566	1.74	-2521.8
-1.5	1.608	28.41	-204.4	-1.5	1.591	1.73	-2574.3
-2.0	1.644	28.29	-248.1	-2.0	1.615	1.71	-2623.5
-2.5	1.680	28.16	-298.0	-2.5	1.639	1.69	-2674.1
-3.0	1.716	28.02	-352.8	-3.0	1.663	1.67	-2720.5

The CC-m_1m_1 molecule in the 93rd vibrational mode:



The CC-$\beta_1\beta_1$ molecule in the 88th vibrational mode:

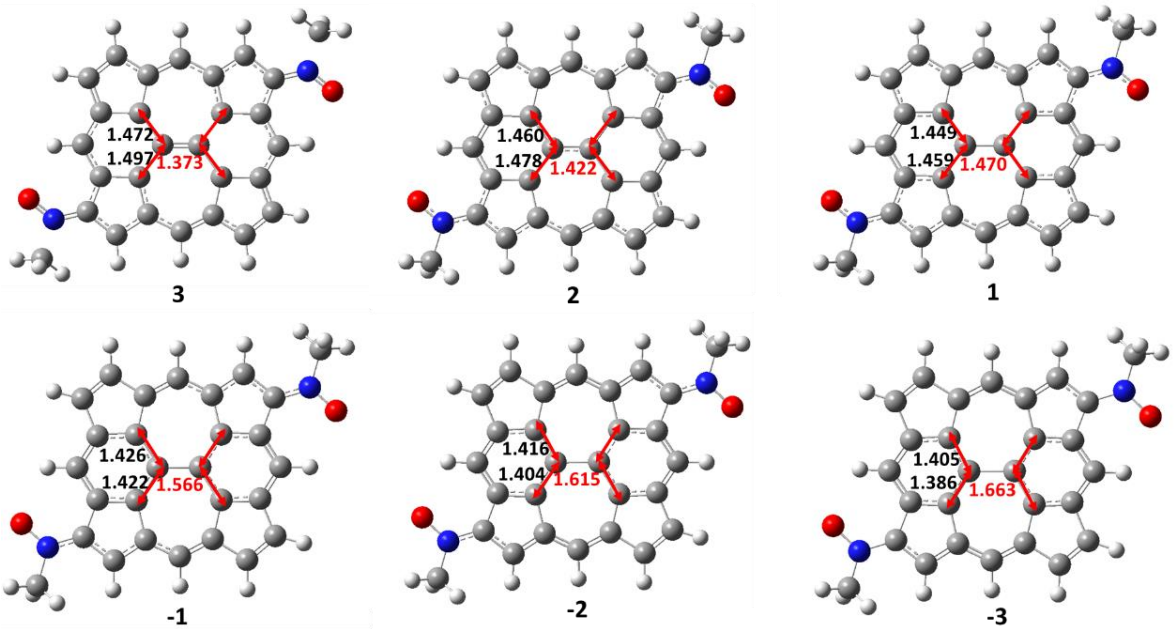
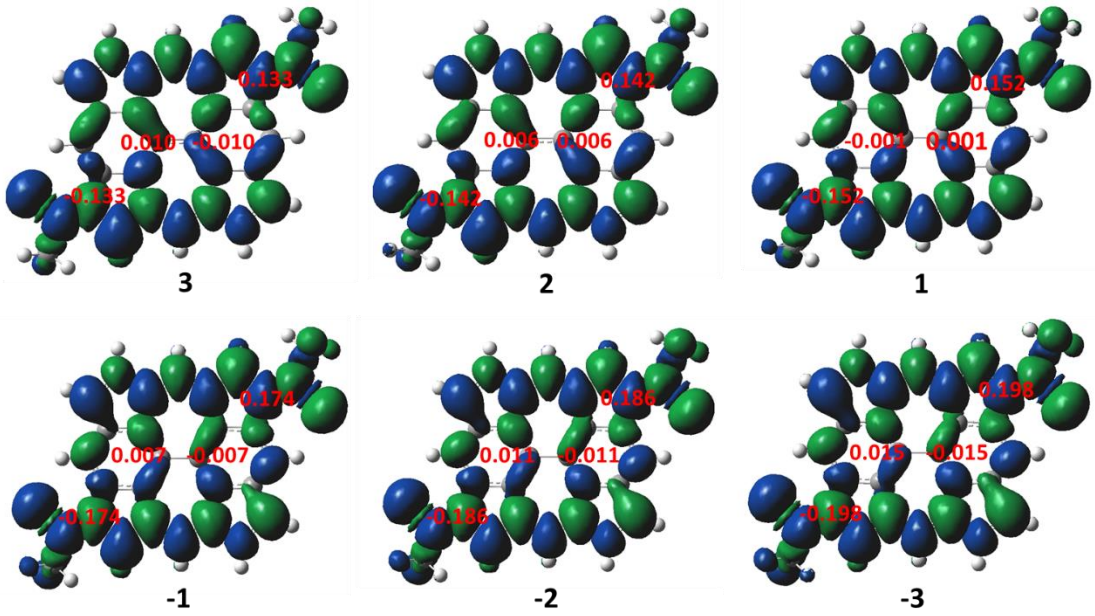


Figure S11. Relevant snapshot configurations of CC-m_1m_1 in the 93rd vibrational mode and CC-$\beta_1\beta_1$ in the 88th vibrational mode (n = -3∼3).

The CC-m_1m_1 molecule in the 93rd vibrational mode:



The CC-$\beta_1\beta_1$ molecule in the 88th vibrational mode:

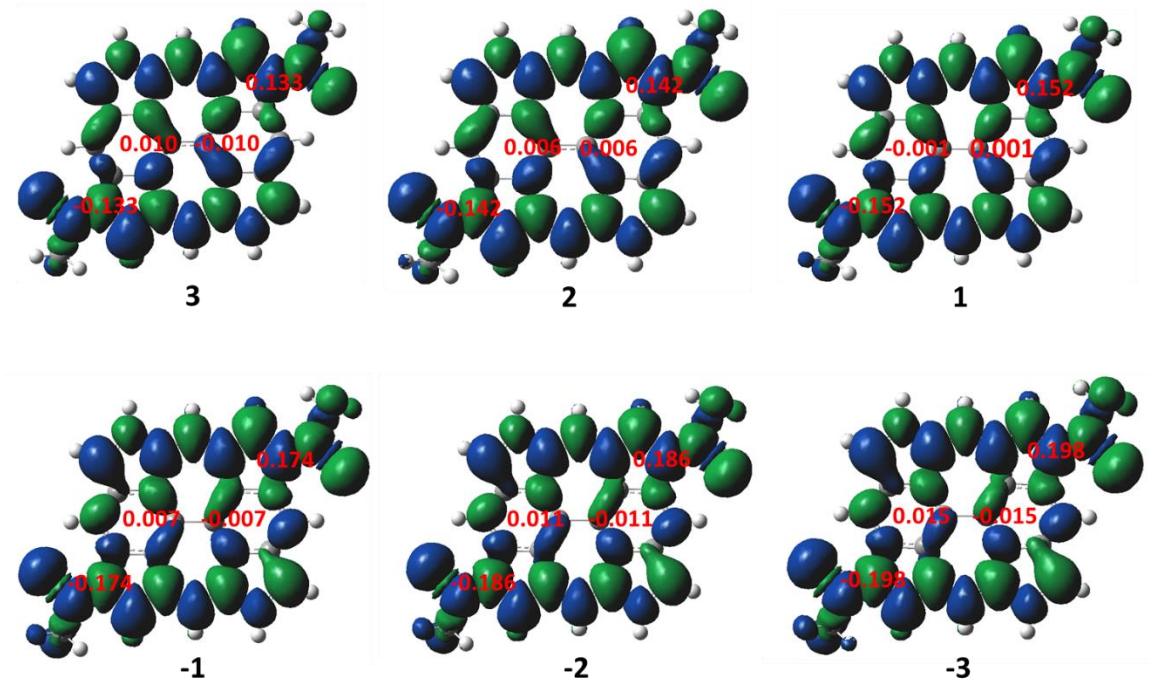


Figure S12. Spin density maps (isovalues =0.0004) of CC-m_1m_1 in the 93rd vibrational mode and CC-$\beta_1\beta_1$ in the 88th vibrational mode (n = -3~3).

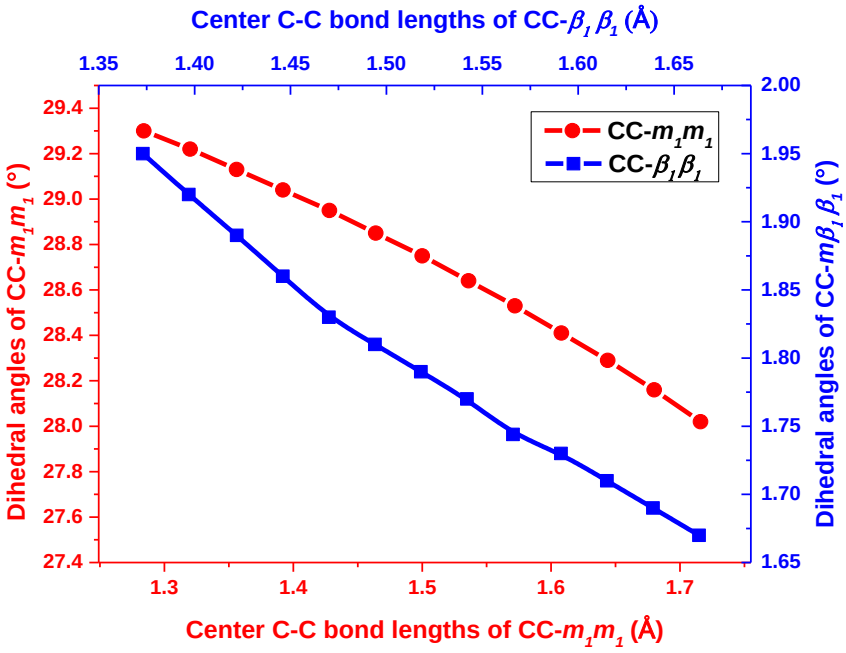


Figure S13. Relationship between dihedral angles and center C-C bond lengths for the CC-m_1m_1 and CC-$\beta_1\beta_1$ molecules (n=-3~3).

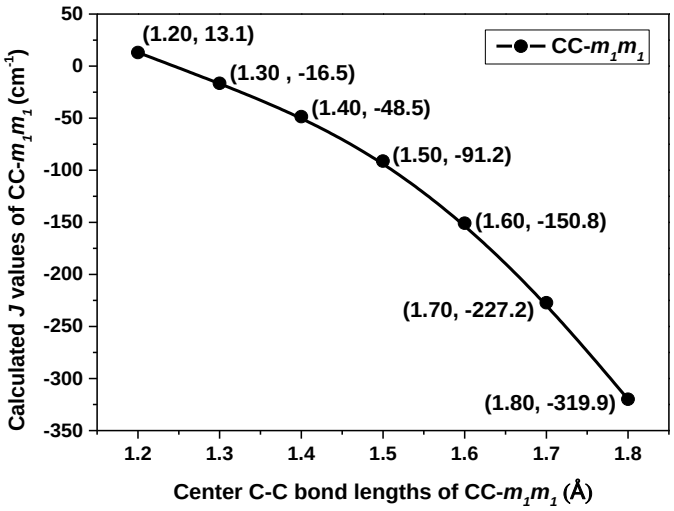


Figure S14. Relationship between the *J* values and center C-C bond lengths in the CC-m_1m_1 molecule calculated from the optimized geometries with different center C-C bond lengths.

9. Figures and Data for the BB-Cored-2e Molecules

Table S8. Total Energies of the CS, BS and T States, Corresponding $<S^2>$ and *J* Values of Diradicals Calculated at the (U)B3LYP/6-311G(d, p) Level.

BB-cored-2e	**$E_{(CS)}$**	**$E_{(BS)}$ ($<S^2>$)**	**$E_{(T)}$ ($<S^2>$)**	***J*** (cm^{-1})
BB-m_1m_1-2e	-1310.2359658	-1310.2376745 (0.721)	-1310.2247123 (2.030)	-943.5
BB-$\beta_1\beta_1$-2e	-1310.244353	-1310.2531309 (0.980)	-1310.2505212 (2.038)	-521.6
BB-$\beta_2\beta_2$-2e	-1310.2289209	-1310.2468681 (1.032)	-1310.2462467 (2.044)	-134.8
BB-m_2m_2-2e	-1310.2009454	-1310.2171434 (1.010)	-1310.2171149 (2.009)	-6.3
BB-$m_1\beta_1$-2e	-1310.2356469	-1310.2438566 (0.984)	-1310.2423736 (2.047)	-306.2
BB-$\beta_1\beta_2$-2e	-1310.2338202	-1310.2487768 (1.018)	-1310.248445 (2.052)	-70.4
BB-$m_1\beta_2$-2e	-1310.2184453	-1310.2391386 (1.028)	-1310.2400174 (2.057)	189.3
BB-m_1m_2-2e	-1310.2085409	-1310.2245 (1.024)	-1310.225 (2.030)	46.3
BB-$m_2\beta_1$-2e	-1310.1984207	-1310.2340841 (1.027)	-1310.2342999 (2.034)	47.1
BB-$m_2\beta_2$-2e	-1310.1435309	-1310.2319947 (1.021)	-1310.2315659 (2.027)	-93.5

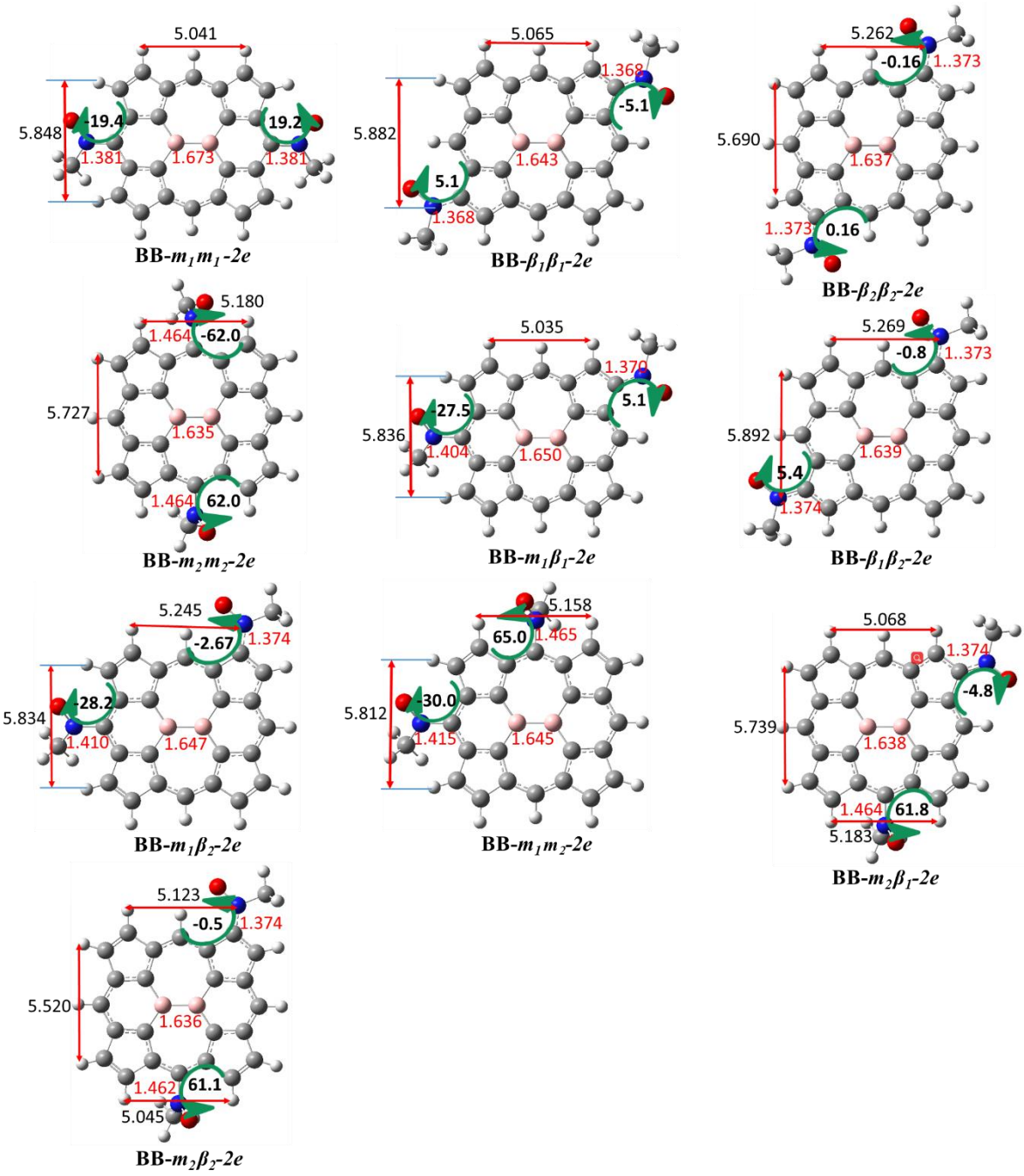


Figure S15. The Optimized molecular geometries with dihedral angles and major bond lengths about the diradical molecules in more stable spin states calculated at the UB3LYP/6-311G (d,p) level.

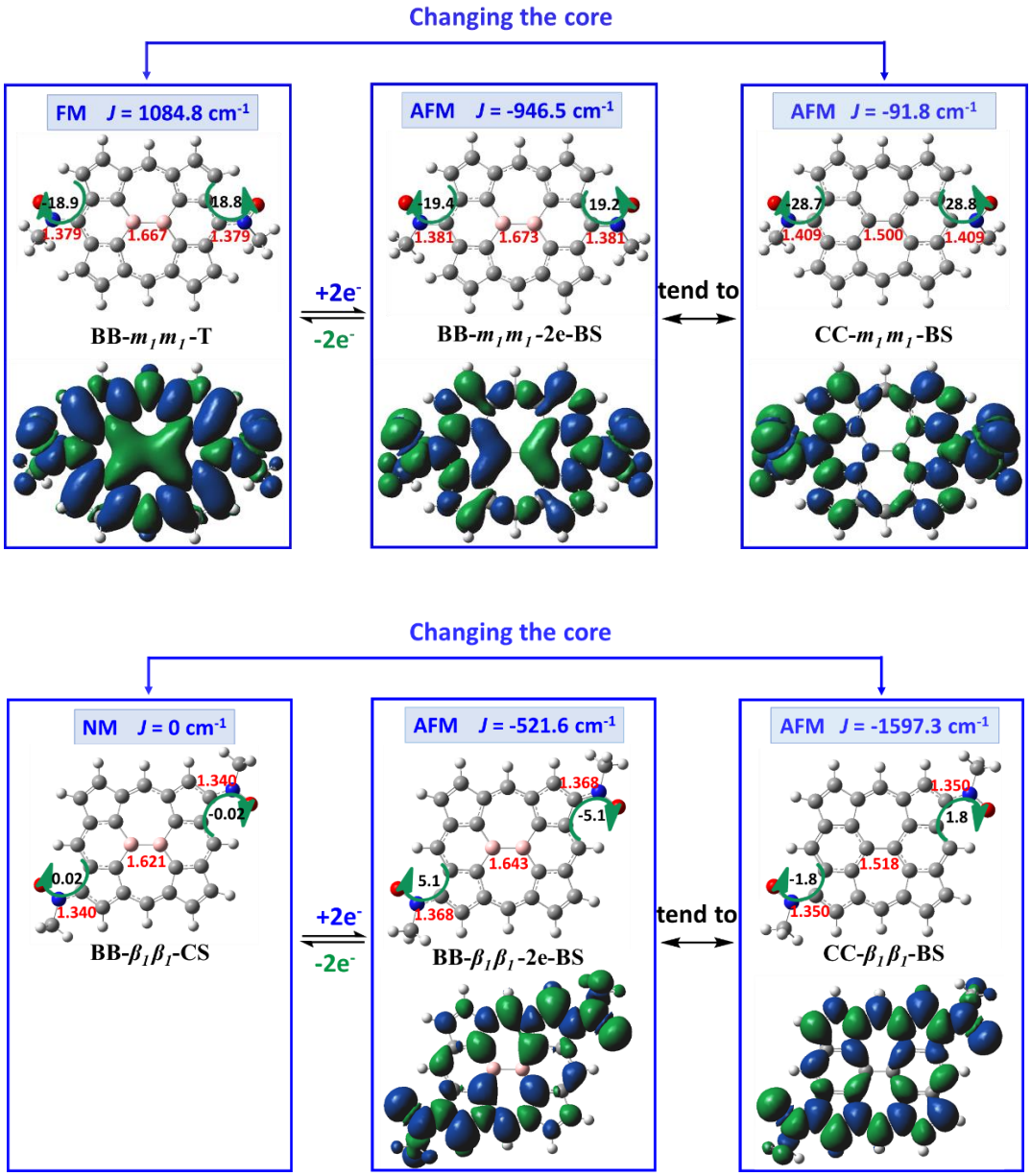


Figure S16. Structural effects and the spin density maps (isovalues = 0.0004).

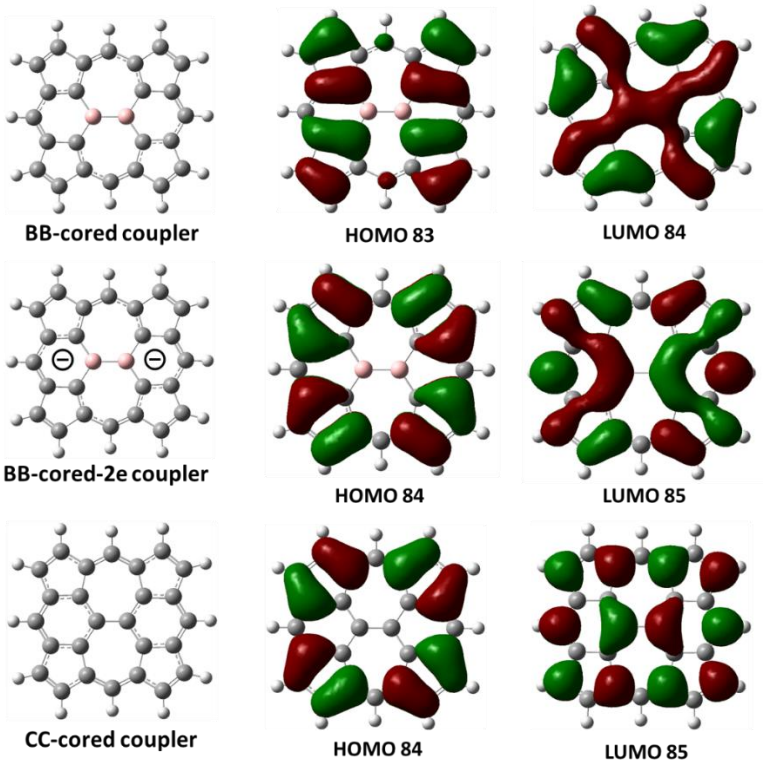


Figure S17. HOMO and LUMO characters of different couplers.