

SUPPORTING INFORMATION

Strategies for Design of Potential Singlet Fission Chromophores Utilizing a Combination of Ground State and Excited State Aromaticity Rules

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CHOICE OF COMPUTATIONAL METHOD

Choosing the method for computing excitation energies is important. Kaupp and co-workers used a TD-DFT-based protocol for the screening of singlet fission chromophores, and they proposed vertical excitation energies computed with local hybrid functionals.^{S1} Yet, M06-2X was found to perform similarly, and we used this functional as we showed earlier that it gives good T_1 state geometries for substituted fulvenes when compared to the T_1 state geometries calculated with CASPT2. We first used the computational scheme derived by Zeng, Hoffmann, and Ananth which gives the correct ordering of the T_1 , S_1 , and T_2 states of pentacene.^{S2} This approach uses adiabatic excitations to the T_1 state and vertical excitations to the S_1 (T_2) states from the S_0 (T_1) optimized structures. Additionally, the vertical excitations to the T_1 state were computed for most of the compounds. To assess the performance of M06-2X in the present study we compare experimental excitation energies of two compounds known to undergo singlet fission; pentacene and 1,3-diphenylisobenzofuran (DPB). The same energy ordering is obtained with the M06-2X based protocol as in the experiments. Moreover, both singlet fission criteria are satisfied for pentacene and nearly satisfied in case of DPB, which reveals that M06-2X should be a suitable method. For benzene and CBD, the arrangement of the electronic excited states is the same in both methods.

NICS-XY scans have also been carried out using B3LYP and CAM-B3LYP, apart from M06-2X, in order for us to see how the different amounts of exact exchange as well as range-corrections impacted on the NICS-XY scans of extensively π -conjugated compounds.

Table S1. Electronic excitation energies (eV) of cyclobutadiene (CBD), benzene, pentacene and 1,3-diphenylisobenzofuran (DPB) computed at TD-M06-2X/def2-TZVPD//M06-2X/6-311+G(d,p) and, in parenthesis, CASPT2/ANO-RCC-VDZP//M06-2X/6-311+G(d,p) levels.

Compound	$E(T_1)^a$	$S_1^{b_v}$	T_2^b	$E(S_1)/E(T_1)$	$E(T_2)/E(S_1)$
CBD ^c	0.51 (0.49)	2.70 (2.94)	4.69 (5.27)	5.29 (6.00)	1.66 (1.79)
Benzene ^c	4.49 (3.96)	5.57 (5.09)	6.64 (6.10)	1.24 (1.29)	1.19 (1.20)
Pentacene ^d	0.98 (0.86)	2.28 (2.30)	2.38 (>2.00)	2.33 (2.67)	1.04 (0.87)
DPB ^d	1.64 (1.41)	3.22 (3.01)	3.58 (3.16)	1.96 (2.13)	1.11 (1.05)

^a T_1 adiabatic excitation energies computed at the M06-2X or CASPT2 triplet optimized geometry depending on the system.

^b S_1 (T_2) vertical excitations computed from the S_0 (T_1) optimized geometry.

^c Energies in parenthesis computed at the CASPT2/ANO-RCC-VDZP level.

^d Energies in parenthesis correspond to experimental data (for pentacene see ref. ^{S3} and, for DPB see ref. ^{S4, S5}).

FULVENES

Table S2. The $E(T_1)_v$, $E(T_1)_a$, $E(S_1)$ and $E(T_2)$ of the differently substituted fulvenes sorted by substituents X and Y. The label “REARRANGED” means that the optimal structure is not the one expected due to the rearrangement of the substituents or the formation of chemical bonds between substituents. Such cases are therefore not corresponding to original fulvenic structures.

		$E(T_1)_v$	$E(T_1)_a$	$E(S_1)$	$E(T_2)$	$E(S_1)/E(T_1)$	$E(T_2)/E(S_1)$	$E(T_2)/E(T_1)$
X=H	Y = H	2.53	1.72	3.64	3.20	2.12	0.88	1.86
X = BF ₂	Y = BF ₂	2.22	1.39	3.31	2.63	2.39	0.79	1.89
	Y = BH ₂	2.03	1.13	3.23	3.39	2.85	1.05	2.99
	Y = CF ₃	2.46	1.45	3.57	2.36	2.46	0.66	1.62
	Y = Cl	2.08	1.07	3.03	2.73	2.83	0.90	2.55
	Y = CN	2.15	1.30	3.32	2.53	2.56	0.76	1.95
	Y = F	1.86	0.83	2.74	2.90	3.30	1.06	3.49
	Y = Me	1.91	0.92	2.74	2.63	2.98	0.96	2.86
	Y = NH ₂	REARRANGED						
	Y = NMe ₂	REARRANGED						
	Y = NO ₂	REARRANGED						
X = BH ₂	Y = OH	1.89	0.72	2.78	3.81	3.84	1.37	5.26
	Y = OMe	1.93	0.83	2.79	3.89	3.37	1.39	4.71
	Y = SH	2.35	0.92	3.40	3.02	3.68	0.89	3.27
	Y = SiH ₃	2.04	1.21	2.91	2.52	2.41	0.87	2.09
	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene						
	Y = BH ₂	REARRANGED						
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene						
	Y = Cl	2.43	1.28	3.42	2.93	2.67	0.86	2.29
	Y = CN	2.39	1.53	3.59	2.69	2.35	0.75	1.76
	Y = F	2.39	0.88	3.39	2.82	3.87	0.83	3.23
	Y = Me	Degenerate states						
	Y = NH ₂	REARRANGED						
	Y = NMe ₂	REARRANGED						
	Y = NO ₂	REARRANGED						
	Y = OH	S ₁ state has charge transfer char. as LUMO is localized on X subst.						
	Y = OMe	2.29	0.87	3.17	3.01	3.65	0.95	3.46
	Y = SH	REARRANGED						
	Y = SiH ₃	REARRANGED						
X = Cl	Y = BF ₂	2.38	1.73	3.56	2.78	2.06	0.78	1.61
	Y = BH ₂	2.21	1.59	3.47	2.77	2.18	0.80	1.74
	Y = CF ₃	2.59	1.83	3.70	2.79	2.02	0.76	1.53
	Y = Cl	2.06	1.31	2.97	2.92	2.27	0.98	2.23
	Y = CN	2.14	1.55	3.25	2.83	2.09	0.87	1.82
	Y = F	2.13	1.27	3.07	3.22	2.41	1.05	2.53
	Y = Me	2.25	1.46	3.18	3.05	2.18	0.96	2.10

	Y = NH ₂	1.62	0.64	2.42	3.29	3.81	1.36	5.17
	Y = NMe ₂	1.81	0.97	2.56	3.38	2.65	1.32	3.50
	Y = NO ₂	2.33	1.65	3.37	2.57	2.04	0.76	1.56
	Y = OH	1.85	1.06	2.70	3.32	2.54	1.23	3.12
	Y = OMe	1.93	1.19	2.76	3.30	2.32	1.20	2.78
	Y = SH	1.67	1.02	2.47	3.13	2.42	1.27	3.06
	Y = SiH ₃	2.45	1.72	3.47	2.93	2.02	0.84	1.70
X = CN	Y = BF ₂	2.06	1.31	3.01	2.45	2.29	0.81	1.86
	Y = BH ₂	1.94	1.24	2.98	3.04	2.40	1.02	2.45
	Y = CF ₃	2.13	1.36	3.03	2.44	2.23	0.81	1.80
	Y = Cl	1.49	0.78	2.23	2.61	2.87	1.17	3.36
	Y = CN	1.72	1.10	2.63	2.39	2.40	0.91	2.18
	Y = F	1.54	0.72	2.32	2.72	3.21	1.17	3.77
	Y = Me	1.63	0.90	2.36	2.69	2.61	1.14	2.97
	Y = NH ₂	T ₀ ground state						
	Y = NMe ₂	1.03	0.21	1.63	3.41	7.77	2.10	16.29
	Y = NO ₂	1.99	1.25	2.91	2.41	2.32	0.83	1.93
	Y = OH	1.19	0.45	1.89	2.84	4.20	1.50	6.30
	Y = OMe	1.22	0.53	1.90	2.86	3.59	1.50	5.40
	Y = SH	0.98	0.38	1.62	2.70	4.24	1.67	7.08
	Y = SiH ₃	1.93	1.23	2.73	2.54	2.22	0.93	2.06
X = F	Y = BF ₂	2.62	2.03	4.02	3.09	1.98	0.77	1.52
	Y = BH ₂	2.25	1.82	3.78	2.85	2.08	0.76	1.57
	Y = CF ₃	2.88	2.12	4.18	3.36	1.97	0.80	1.58
	Y = Cl	2.43	1.66	3.51	3.27	2.11	0.93	1.96
	Y = CN	2.40	1.82	3.70	3.27	2.03	0.88	1.79
	Y = F	2.52	1.60	3.64	3.29	2.28	0.91	2.07
	Y = Me	2.61	1.76	3.72	3.13	2.12	0.84	1.78
	Y = NH ₂	2.00	0.93	2.94	3.31	3.17	1.12	3.57
	Y = NMe ₂	2.18	1.23	3.07	3.39	2.49	1.10	2.74
	Y = NO ₂	Not a clear HOMO-to-LUMO excitation						
	Y = OH	2.28	1.39	3.29	3.34	2.37	1.02	2.41
	Y = OMe	2.36	1.50	3.34	3.31	2.23	0.99	2.21
	Y = SH	2.09	1.35	3.02	3.16	2.24	1.04	2.33
	Y = SiH ₃	2.73	2.01	3.94	3.13	1.96	0.79	1.55
X = H	Y = BF ₂	2.43	1.83	3.76	2.85	2.06	0.76	1.56
	Y = BH ₂	LUMO primarily localized on the Y substituents						
	Y = CF ₃	2.66	1.88	3.87	3.07	2.06	0.79	1.64
	Y = Cl	2.18	1.43	3.18	3.29	2.22	1.04	2.30
	Y = CN	2.22	1.61	3.45	3.02	2.13	0.88	1.87
	Y = F	2.21	1.36	3.24	3.45	2.38	1.06	2.53
	Y = Me	2.31	1.53	3.31	3.35	2.16	1.01	2.18
	Y = NH ₂	1.74	0.87	2.59	3.70	2.98	1.43	4.27
	Y = NMe ₂	1.93	1.09	2.76	3.65	2.52	1.32	3.34

	Y = NO ₂	2.31	1.70	3.58	2.71	2.10	0.76	1.59
	Y = OH	1.97	1.08	2.89	3.74	2.67	1.29	3.45
	Y = OMe	2.05	1.32	2.94	3.56	2.23	1.21	2.70
	Y = SH	2.06	1.22	2.98	3.46	2.44	1.16	2.83
	Y = SiH ₃	2.51	1.78	3.62	3.14	2.03	0.87	1.76
X = Me	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene						
	Y = BH ₂	LUMO primarily localized on the Y substituents						
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene						
	Y = Cl	2.30	1.52	3.28	2.99	2.15	0.91	1.96
	Y = CN	2.31	1.75	3.54	2.90	2.03	0.82	1.66
	Y = F	2.38	1.53	3.41	3.41	2.23	1.00	2.22
	Y = Me	2.46	1.62	3.46	3.04	2.14	0.88	1.88
	Y = NH ₂	1.96	0.99	2.83	3.32	2.84	1.18	3.34
	Y = NMe ₂	2.13	1.18	2.97	3.06	2.51	1.03	2.59
	Y = NO ₂	Not a clear HOMO-to-LUMO excitation						
	Y = OH	2.14	1.29	3.07	3.48	2.39	1.13	2.70
	Y = OMe	2.24	1.49	3.14	3.41	2.11	1.08	2.29
	Y = SH	1.99	1.29	2.86	3.09	2.21	1.08	2.39
	Y = SiH ₃	2.64	1.92	3.75	2.96	1.95	0.79	1.54
X = NH ₂	Y = BF ₂	REARRANGED						
	Y = BH ₂	REARRANGED						
	Y = CF ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = Cl	2.97	2.26	3.93	3.71	1.74	0.94	1.64
	Y = CN	LUMO primarily localized on the Y substituents						
	Y = F	3.01	2.20	4.01	3.86	1.82	0.96	1.76
	Y = Me	2.92	2.25	3.92	3.59	1.74	0.92	1.59
	Y = NH ₂	T ₁ excitation is different to that of the parent fulvene						
	Y = NMe ₂	Not a clear HOMO-to-LUMO excitation						
	Y = NO ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = OH	Not a clear HOMO-to-LUMO excitation						
	Y = OMe	Not a clear HOMO-to-LUMO excitation						
	Y = SH	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = SiH ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
X = NMe ₂	Y = BF ₂	REARRANGED						
	Y = BH ₂	REARRANGED						
	Y = CF ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = Cl	2.93	2.20	3.68	3.46	1.67	0.94	1.57
	Y = CN	LUMO primarily localized on the Y substituents						
	Y = F	2.94	2.14	3.80	3.59	1.78	0.95	1.68
	Y = Me	2.78	1.97	3.58	3.16	1.81	0.88	1.60
	Y = NH ₂	2.37	1.23	3.04	3.94	2.46	1.30	3.20
	Y = NMe ₂	2.56	1.69	3.20	3.38	1.90	1.05	2.00
	Y = NO ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = OH	T ₁ excitation is different to that of the parent fulvene						

	Y = OMe	T ₁ excitation is different to that of the parent fulvene						
	Y = SH	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = SiH ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
X = NO ₂	Y = BF ₂	2.11	0.67	3.06	3.08	4.57	1.01	4.60
	Y = BH ₂	REARRANGED						
	Y = CF ₃	2.24	1.30	3.22	2.43	2.48	0.76	1.87
	Y = Cl	1.70	0.79	2.49	2.58	3.16	1.04	3.27
	Y = CN	1.86	1.16	2.84	2.61	2.46	0.92	2.26
	Y = F	1.70	0.73	2.52	2.85	3.44	1.13	3.90
	Y = Me	1.78	0.85	2.54	2.67	2.98	1.05	3.15
	Y = NH ₂	Not a clear HOMO-to-LUMO excitation						
	Y = NMe ₂	1.65	0.10	2.33	2.92	23.80	1.25	29.83
	Y = NO ₂	2.10	1.29	3.09	2.34	2.40	0.76	1.82
	Y = OH	1.43	0.44	2.17	2.86	4.94	1.31	6.49
	Y = OMe	1.46	0.50	2.17	2.86	4.32	1.32	5.70
	Y = SH	1.50	0.45	2.19	2.82	4.84	1.29	6.23
	Y = SiH ₃	2.00	1.18	2.81	2.76	2.39	0.98	2.34
X = OH	Y = BF ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = BH ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene						
	Y = Cl	2.49	1.76	3.52	3.50	2.00	0.99	1.99
	Y = CN	LUMO primarily localized on the Y substituents						
	Y = F	2.57	1.72	3.63	3.67	2.11	1.01	2.13
	Y = Me	2.63	1.85	3.69	3.49	2.00	0.94	1.89
	Y = NH ₂	1.98	1.06	2.87	3.50	2.70	1.22	3.30
	Y = NMe ₂	HOMO is of a different character compared to that of the parent fulvene						
	Y = NO ₂	REARRANGED						
	Y = OH	2.69	1.94	3.69	3.86	1.90	1.05	1.99
	Y = OMe	2.41	1.48	3.34	3.25	2.26	0.97	2.19
	Y = SH	2.16	1.48	3.06	3.53	2.08	1.15	2.39
	Y = SiH ₃	LUMO primarily localized on the Y substituents						
Y=H	Y = BF ₂	1.91	1.13	2.75	2.87	2.43	1.04	2.54
	Y = BH ₂	1.88	1.06	2.64	2.60	2.49	0.99	2.45
	Y = CF ₃	2.16	1.34	3.13	3.10	2.33	0.99	2.31
	Y = Cl	2.42	1.60	3.44	2.93	2.15	0.85	1.83
	Y = CN	1.91	1.14	2.74	2.52	2.41	0.92	2.21
	Y = F	2.79	1.94	4.00	3.05	2.06	0.76	1.57
	Y = Me	2.64	1.85	3.75	3.11	2.03	0.83	1.68
	Y = NH ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene						
	Y = NMe ₂	T ₁ excitation is different to that of the parent fulvene						
	Y = NO ₂	1.96	1.13	2.80	2.90	2.47	1.03	2.56
	Y = OH	2.80	2.00	3.94	3.33	1.97	0.85	1.66
	Y = OMe	3.03	1.99	4.15	3.29	2.09	0.79	1.66
	Y = SH	2.44	1.63	3.41	2.85	2.08	0.84	1.74

	Y = SiH ₃	2.30	1.46	3.27	2.90	2.24	0.89	1.99
X=SH	Y = BF ₂	Both T1 and S1 excitations are different to that of the parent fulvene						
	Y = BH ₂	Both T1 and S1 excitations are different to that of the parent fulvene						
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene						
	Y = Cl	2.22	1.41	3.07	2.73	2.17	0.89	1.93
	Y = CN	T ₁ excitation is different to that of the parent fulvene						
	Y = F	2.33	1.46	3.23	3.14	2.22	0.97	2.16
	Y = Me	2.30	1.40	3.16	2.79	2.25	0.88	1.99
	Y = NH ₂	2.05	0.66	2.86	3.33	4.36	1.17	5.08
	Y = NMe ₂	Not a clear HOMO-to-LUMO excitation						
	Y = NO ₂	2.09	1.68	3.32	2.92	1.98	0.88	1.74
	Y = OH	2.09	1.29	2.92	3.15	2.25	1.08	2.43
	Y = OMe	2.18	1.42	2.99	3.10	2.11	1.04	2.18
	Y = SH	1.81	1.05	2.54	2.76	2.43	1.09	2.64
	Y = SiH ₃	LUMO is of a different character compared to that of the parent fulvene						
X=CF ₃	Y = BF ₂	2.20	1.33	3.27	2.83	2.47	0.87	2.13
	Y = BH ₂	2.10	1.35	3.23	3.26	2.40	1.01	2.42
	Y = CF ₃	2.26	1.33	3.29	1.95	2.48	0.59	1.47
	Y = Cl	1.68	0.84	2.50	2.59	2.96	1.04	3.07
	Y = CN	1.90	1.22	2.94	2.66	2.41	0.91	2.18
	Y = F	1.77	0.86	2.65	3.01	3.08	1.13	3.49
	Y = Me	1.81	0.94	2.63	2.75	2.79	1.05	2.92
	Y = NH ₂	T ₀ ground state						
	Y = NMe ₂	1.46	0.22	2.14	2.72	9.67	1.28	12.32
	Y = NO ₂	2.18	1.38	3.25	2.44	2.35	0.75	1.76
	Y = OH	1.44	0.57	2.23	2.99	3.91	1.34	5.24
	Y = OMe	1.48	0.66	2.23	3.00	3.39	1.35	4.56
	Y = SH	1.60	0.61	2.38	2.81	3.90	1.18	4.59
	Y = SiH ₃	2.16	1.40	3.10	2.82	2.21	0.91	2.01
X=OMe	Y = BF ₂	LUMO primarily localized on the Y substituents						
	Y = BH ₂	HOMO and LUMO primarily localized on the Y substituents						
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene						
	Y = CN	2.54	1.97	3.75	3.22	1.91	0.86	1.64
	Y = Cl	2.45	1.71	3.44	3.41	2.01	0.99	1.99
	Y = F	2.79	1.82	3.80	3.84	2.09	1.01	2.11
	Y = Me	2.57	1.79	3.60	3.42	2.01	0.95	1.91
	Y = NH ₂	1.95	1.03	2.81	3.44	2.74	1.22	3.35
	Y = NMe ₂	2.32	1.34	3.18	3.37	2.37	1.06	2.52
	Y = NO ₂	T ₁ excitation is different to that of the parent fulvene						
	Y = OH	Not a clear HOMO-to-LUMO excitation						
	Y = OMe	Not a clear HOMO-to-LUMO excitation						
	Y = SH	2.13	1.45	3.00	3.46	2.07	1.15	2.39
	Y = SiH ₃	2.72	2.02	3.84	3.21	1.90	0.83	1.59
X=SiH ₃	Y = BF ₂	2.34	1.65	3.50	2.40	2.12	0.69	1.45

Y = BH ₂	REARRANGED						
Y = CF ₃	2.47	1.63	3.55	2.44	2.18	0.69	1.50
Y = CN	2.09	1.46	3.19	2.58	2.19	0.81	1.77
Y = Cl	1.95	1.16	2.82	2.72	2.43	0.97	2.34
Y = F	1.99	1.12	2.89	3.16	2.58	1.09	2.82
Y = Me	2.02	1.20	2.87	2.77	2.39	0.97	2.31
Y = NH ₂	1.69	0.52	2.44	3.11	4.67	1.27	5.94
Y = NMe ₂	1.88	0.98	2.58	3.39	2.62	1.31	3.45
Y = NO ₂	Not a clear HOMO-to-LUMO excitation						
Y = OH	1.72	0.91	2.52	3.22	2.77	1.28	3.55
Y = OMe	1.78	1.01	2.55	3.28	2.53	1.28	3.24
Y = SH	2.22	0.93	3.17	2.71	3.40	0.86	2.91
Y = SiH ₃	2.32	1.51	3.28	2.67	2.17	0.81	1.77

Table S3. The $E(T_1)_v$, $E(T_1)_a$, $E(S_1)$ and $E(T_2)$ of the differently substituted fulvenes sorted by $E(T_1)_a$. For label “REARRANGED” see Table S2.

		$E(T_1)_v$	$E(T_1)_a$	$E(S_1)$	$E(T_2)$	$E(S_1)/E(T_1)$	$E(T_2)/E(S_1)$	$E(T_2)/E(T_1)$
X = NO ₂	Y = NMe ₂	1.65	0.10	2.33	2.92	23.80	1.25	29.83
X = CN	Y = NMe ₂	1.03	0.21	1.63	3.41	7.77	2.10	16.29
X = CF ₃	Y = NMe ₂	1.46	0.22	2.14	2.72	9.67	1.28	12.32
X = CN	Y = SH	0.98	0.38	1.62	2.70	4.24	1.67	7.08
X = NO ₂	Y = OH	1.43	0.44	2.17	2.86	4.94	1.31	6.49
X = CN	Y = OH	1.19	0.45	1.89	2.84	4.20	1.50	6.30
X = NO ₂	Y = SH	1.50	0.45	2.19	2.82	4.84	1.29	6.23
X = NO ₂	Y = OMe	1.46	0.50	2.17	2.86	4.32	1.32	5.70
X = SiH ₃	Y = NH ₂	1.69	0.52	2.44	3.11	4.67	1.27	5.94
X = CN	Y = OMe	1.22	0.53	1.90	2.86	3.59	1.50	5.40
X = CF ₃	Y = OH	1.44	0.57	2.23	2.99	3.91	1.34	5.24
X = CF ₃	Y = SH	1.60	0.61	2.38	2.81	3.90	1.18	4.59
X = Cl	Y = NH ₂	1.62	0.64	2.42	3.29	3.81	1.36	5.17
X = SH	Y = NH ₂	2.05	0.66	2.86	3.33	4.36	1.17	5.08
X = CF ₃	Y = OMe	1.48	0.66	2.23	3.00	3.39	1.35	4.56
X = NO ₂	Y = BF ₂	2.11	0.67	3.06	3.08	4.57	1.01	4.60
X = CN	Y = F	1.54	0.72	2.32	2.72	3.21	1.17	3.77
X = BF ₂	Y = OH	1.89	0.72	2.78	3.81	3.84	1.37	5.26
X = NO ₂	Y = F	1.70	0.73	2.52	2.85	3.44	1.13	3.90
X = CN	Y = Cl	1.49	0.78	2.23	2.61	2.87	1.17	3.36
X = NO ₂	Y = Cl	1.70	0.79	2.49	2.58	3.16	1.04	3.27
X = BF ₂	Y = OMe	1.93	0.83	2.79	3.89	3.37	1.39	4.71
X = BF ₂	Y = F	1.86	0.83	2.74	2.90	3.30	1.06	3.49
X = CF ₃	Y = Cl	1.68	0.84	2.50	2.59	2.96	1.04	3.07
X = NO ₂	Y = Me	1.78	0.85	2.54	2.67	2.98	1.05	3.15
X = CF ₃	Y = F	1.77	0.86	2.65	3.01	3.08	1.13	3.49
X = H	Y = NH ₂	1.74	0.87	2.59	3.70	2.98	1.43	4.27
X = BH ₂	Y = OMe	2.29	0.87	3.17	3.01	3.65	0.95	3.46
X = BH ₂	Y = F	2.39	0.88	3.39	2.82	3.87	0.83	3.23
X = CN	Y = Me	1.63	0.90	2.36	2.69	2.61	1.14	2.97
X = SiH ₃	Y = OH	1.72	0.91	2.52	3.22	2.77	1.28	3.55
X = BF ₂	Y = Me	1.91	0.92	2.74	2.63	2.98	0.96	2.86
X = BF ₂	Y = SH	2.35	0.92	3.40	3.02	3.68	0.89	3.27
X = F	Y = NH ₂	2.00	0.93	2.94	3.31	3.17	1.12	3.57
X = SiH ₃	Y = SH	2.22	0.93	3.17	2.71	3.40	0.86	2.91
X = CF ₃	Y = Me	1.81	0.94	2.63	2.75	2.79	1.05	2.92
X = Cl	Y = NMe ₂	1.81	0.97	2.56	3.38	2.65	1.32	3.50
X = SiH ₃	Y = NMe ₂	1.88	0.98	2.58	3.39	2.62	1.31	3.45
X = Me	Y = NH ₂	1.96	0.99	2.83	3.32	2.84	1.18	3.34
X = SiH ₃	Y = OMe	1.78	1.01	2.55	3.28	2.53	1.28	3.24

X = Cl	Y = SH	1.67	1.02	2.47	3.13	2.42	1.27	3.06
X = OMe	Y = NH ₂	1.95	1.03	2.81	3.44	2.74	1.22	3.35
X = SH	Y = SH	1.81	1.05	2.54	2.76	2.43	1.09	2.64
Y = H	Y = BH ₂	1.88	1.06	2.64	2.60	2.49	0.99	2.45
X = OH	Y = NH ₂	1.98	1.06	2.87	3.50	2.70	1.22	3.30
X = Cl	Y = OH	1.85	1.06	2.70	3.32	2.54	1.23	3.12
X = BF ₂	Y = Cl	2.08	1.07	3.03	2.73	2.83	0.90	2.55
X = H	Y = OH	1.97	1.08	2.89	3.74	2.67	1.29	3.45
X = H	Y = NMe ₂	1.93	1.09	2.76	3.65	2.52	1.32	3.34
X = CN	Y = CN	1.72	1.10	2.63	2.39	2.40	0.91	2.18
X = SiH ₃	Y = F	1.99	1.12	2.89	3.16	2.58	1.09	2.82
Y = H	Y = BF ₂	1.91	1.13	2.75	2.87	2.43	1.04	2.54
Y = H	Y = NO ₂	1.96	1.13	2.80	2.90	2.47	1.03	2.56
X = BF ₂	Y = BH ₂	2.03	1.13	3.23	3.39	2.85	1.05	2.99
Y = H	Y = CN	1.91	1.14	2.74	2.52	2.41	0.92	2.21
X = NO ₂	Y = CN	1.86	1.16	2.84	2.61	2.46	0.92	2.26
X = SiH ₃	Y = Cl	1.95	1.16	2.82	2.72	2.43	0.97	2.34
X = NO ₂	Y = SiH ₃	2.00	1.18	2.81	2.76	2.39	0.98	2.34
X = Me	Y = NMe ₂	2.13	1.18	2.97	3.06	2.51	1.03	2.59
X = Cl	Y = OMe	1.93	1.19	2.76	3.30	2.32	1.20	2.78
X = SiH ₃	Y = Me	2.02	1.20	2.87	2.77	2.39	0.97	2.31
X = BF ₂	Y = SiH ₃	2.04	1.21	2.91	2.52	2.41	0.87	2.09
X = CF ₃	Y = CN	1.90	1.22	2.94	2.66	2.41	0.91	2.18
X = H	Y = SH	2.06	1.22	2.98	3.46	2.44	1.16	2.83
X = NMe ₂	Y = NH ₂	2.37	1.23	3.04	3.94	2.46	1.30	3.20
X = CN	Y = SiH ₃	1.93	1.23	2.73	2.54	2.22	0.93	2.06
X = F	Y = NMe ₂	2.18	1.23	3.07	3.39	2.49	1.10	2.74
X = CN	Y = BH ₂	1.94	1.24	2.98	3.04	2.40	1.02	2.45
X = CN	Y = NO ₂	1.99	1.25	2.91	2.41	2.32	0.83	1.93
X = Cl	Y = F	2.13	1.27	3.07	3.22	2.41	1.05	2.53
X = BH ₂	Y = Cl	2.43	1.28	3.42	2.93	2.67	0.86	2.29
X = Me	Y = OH	2.14	1.29	3.07	3.48	2.39	1.13	2.70
X = NO ₂	Y = NO ₂	2.10	1.29	3.09	2.34	2.40	0.76	1.82
X = Me	Y = SH	1.99	1.29	2.86	3.09	2.21	1.08	2.39
X = SH	Y = OH	2.09	1.29	2.92	3.15	2.25	1.08	2.43
X = BF ₂	Y = CN	2.15	1.30	3.32	2.53	2.56	0.76	1.95
X = NO ₂	Y = CF ₃	2.24	1.30	3.22	2.43	2.48	0.76	1.87
X = Cl	Y = Cl	2.06	1.31	2.97	2.92	2.27	0.98	2.23
X = CN	Y = BF ₂	2.06	1.31	3.01	2.45	2.29	0.81	1.86
X = H	Y = OMe	2.05	1.32	2.94	3.56	2.23	1.21	2.70
X = CF ₃	Y = BF ₂	2.20	1.33	3.27	2.83	2.47	0.87	2.13
X = CF ₃	Y = CF ₃	2.26	1.33	3.29	1.95	2.48	0.59	1.47
X = OMe	Y = NMe ₂	2.32	1.34	3.18	3.37	2.37	1.06	2.52
Y = H	Y = CF ₃	2.16	1.34	3.13	3.10	2.33	0.99	2.31
X = CF ₃	Y = BH ₂	2.10	1.35	3.23	3.26	2.40	1.01	2.42

X = F	Y = SH	2.09	1.35	3.02	3.16	2.24	1.04	2.33
X = H	Y = F	2.21	1.36	3.24	3.45	2.38	1.06	2.53
X = CN	Y = CF ₃	2.13	1.36	3.03	2.44	2.23	0.81	1.80
X = CF ₃	Y = NO ₂	2.18	1.38	3.25	2.44	2.35	0.75	1.76
X = F	Y = OH	2.28	1.39	3.29	3.34	2.37	1.02	2.41
X = BF ₂	Y = BF ₂	2.22	1.39	3.31	2.63	2.39	0.79	1.89
X = SH	Y = Me	2.30	1.40	3.16	2.79	2.25	0.88	1.99
X = CF ₃	Y = SiH ₃	2.16	1.40	3.10	2.82	2.21	0.91	2.01
X = SH	Y = Cl	2.22	1.41	3.07	2.73	2.17	0.89	1.93
X = SH	Y = OMe	2.18	1.42	2.99	3.10	2.11	1.04	2.18
X = H	Y = Cl	2.18	1.43	3.18	3.29	2.22	1.04	2.30
X = BF ₂	Y = CF ₃	2.46	1.45	3.57	2.36	2.46	0.66	1.62
X = OMe	Y = SH	2.13	1.45	3.00	3.46	2.07	1.15	2.39
X = SiH ₃	Y = CN	2.09	1.46	3.19	2.58	2.19	0.81	1.77
X = Cl	Y = Me	2.25	1.46	3.18	3.05	2.18	0.96	2.10
X = SH	Y = F	2.33	1.46	3.23	3.14	2.22	0.97	2.16
Y = H	Y = SiH ₃	2.30	1.46	3.27	2.90	2.24	0.89	1.99
X = OH	Y = SH	2.16	1.48	3.06	3.53	2.08	1.15	2.39
X = OH	Y = OMe	2.41	1.48	3.34	3.25	2.26	0.97	2.19
X = Me	Y = OMe	2.24	1.49	3.14	3.41	2.11	1.08	2.29
X = F	Y = OMe	2.36	1.50	3.34	3.31	2.23	0.99	2.21
X = SiH ₃	Y = SiH ₃	2.32	1.51	3.28	2.67	2.17	0.81	1.77
X = Me	Y = Cl	2.30	1.52	3.28	2.99	2.15	0.91	1.96
X = BH ₂	Y = CN	2.39	1.53	3.59	2.69	2.35	0.75	1.76
X = Me	Y = F	2.38	1.53	3.41	3.41	2.23	1.00	2.22
X = H	Y = Me	2.31	1.53	3.31	3.35	2.16	1.01	2.18
X = Cl	Y = CN	2.14	1.55	3.25	2.83	2.09	0.87	1.82
X = Cl	Y = BH ₂	2.21	1.59	3.47	2.77	2.18	0.80	1.74
X = F	Y = F	2.52	1.60	3.64	3.29	2.28	0.91	2.07
Y = H	Y = Cl	2.42	1.60	3.44	2.93	2.15	0.85	1.83
X = H	Y = CN	2.22	1.61	3.45	3.02	2.13	0.88	1.87
X = Me	Y = Me	2.46	1.62	3.46	3.04	2.14	0.88	1.88
X = SiH ₃	Y = CF ₃	2.47	1.63	3.55	2.44	2.18	0.69	1.50
Y = H	Y = SH	2.44	1.63	3.41	2.85	2.08	0.84	1.74
X = SiH ₃	Y = BF ₂	2.34	1.65	3.50	2.40	2.12	0.69	1.45
X = Cl	Y = NO ₂	2.33	1.65	3.37	2.57	2.04	0.76	1.56
X = F	Y = Cl	2.43	1.66	3.51	3.27	2.11	0.93	1.96
X = SH	Y = NO ₂	2.09	1.68	3.32	2.92	1.98	0.88	1.74
X = NMe ₂	Y = NMe ₂	2.56	1.69	3.20	3.38	1.90	1.05	2.00
X = H	Y = NO ₂	2.31	1.70	3.58	2.71	2.10	0.76	1.59
X = OMe	Y = Cl	2.45	1.71	3.44	3.41	2.01	0.99	1.99
X = H	X = H	2.53	1.72	3.64	3.20	2.12	0.88	1.86
X = OH	Y = F	2.57	1.72	3.63	3.67	2.11	1.01	2.13
X = Cl	Y = SiH ₃	2.45	1.72	3.47	2.93	2.02	0.84	1.70
X = Cl	Y = BF ₂	2.38	1.73	3.56	2.78	2.06	0.78	1.61

X = Me	Y = CN	2.31	1.75	3.54	2.90	2.03	0.82	1.66
X = F	Y = Me	2.61	1.76	3.72	3.13	2.12	0.84	1.78
X = OH	Y = Cl	2.49	1.76	3.52	3.50	2.00	0.99	1.99
X = H	Y = SiH ₃	2.51	1.78	3.62	3.14	2.03	0.87	1.76
X = OMe	Y = Me	2.57	1.79	3.60	3.42	2.01	0.95	1.91
X = F	Y = BH ₂	2.25	1.82	3.78	2.85	2.08	0.76	1.57
X = OMe	Y = F	2.79	1.82	3.80	3.84	2.09	1.01	2.11
X = F	Y = CN	2.40	1.82	3.70	3.27	2.03	0.88	1.79
X = H	Y = BF ₂	2.43	1.83	3.76	2.85	2.06	0.76	1.56
X = Cl	Y = CF ₃	2.59	1.83	3.70	2.79	2.02	0.76	1.53
Y = H	Y = Me	2.64	1.85	3.75	3.11	2.03	0.83	1.68
X = OH	Y = Me	2.63	1.85	3.69	3.49	2.00	0.94	1.89
X = H	Y = CF ₃	2.66	1.88	3.87	3.07	2.06	0.79	1.64
X = Me	Y = SiH ₃	2.64	1.92	3.75	2.96	1.95	0.79	1.54
Y = H	Y = F	2.79	1.94	4.00	3.05	2.06	0.76	1.57
X = OH	Y = OH	2.69	1.94	3.69	3.86	1.90	1.05	1.99
X = OMe	Y = CN	2.54	1.97	3.75	3.22	1.91	0.86	1.64
X = NMe ₂	Y = Me	2.78	1.97	3.58	3.16	1.81	0.88	1.60
Y = H	Y = OMe	3.03	1.99	4.15	3.29	2.09	0.79	1.66
Y = H	Y = OH	2.80	2.00	3.94	3.33	1.97	0.85	1.66
X = F	Y = SiH ₃	2.73	2.01	3.94	3.13	1.96	0.79	1.55
X = OMe	Y = SiH ₃	2.72	2.02	3.84	3.21	1.90	0.83	1.59
X = F	Y = BF ₂	2.62	2.03	4.02	3.09	1.98	0.77	1.52
X = F	Y = CF ₃	2.88	2.12	4.18	3.36	1.97	0.80	1.58
X = NMe ₂	Y = F	2.94	2.14	3.80	3.59	1.78	0.95	1.68
X = NH ₂	Y = F	3.01	2.20	4.01	3.86	1.82	0.96	1.76
X = NMe ₂	Y = Cl	2.93	2.20	3.68	3.46	1.67	0.94	1.57
X = NH ₂	Y = Me	2.92	2.25	3.92	3.59	1.74	0.92	1.59
X = NH ₂	Y = Cl	2.97	2.26	3.93	3.71	1.74	0.94	1.64

Table S4. Absolute S_0 , T_1 , S_1 and T_2 energies (in a.u.) for the differently substituted fulvenes listed. For label “REARRANGED” see Table S2.

		S_0	T_{1v}	T_{1a}	S_1	T_2
X=H	Y = H	-232.16818	-232.07504	-232.10509	-232.03447	-232.05073
X = BF ₂	Y = BF ₂	-1128.59274	-1128.51119	-1128.54170	-1128.47097	-1128.49622
	Y = BH ₂	-731.24552	-731.17102	-731.20383	-731.12681	-731.12093
	Y = CF ₃	-1354.55364	-1354.46329	-1354.50034	-1354.42243	-1354.46709
	Y = Cl	-1599.57939	-1599.50293	-1599.54005	-1599.46791	-1599.47894
	Y = CN	-864.86817	-864.78923	-864.82049	-864.74607	-864.77522
	Y = F	-878.86766	-878.79925	-878.83710	-878.76690	-878.76099
	Y = Me	-758.99406	-758.92397	-758.96021	-758.89320	-758.89739
	Y = NH ₂	REARRANGED				
	Y = NMe ₂	REARRANGED				
	Y = NO ₂	REARRANGED				
	Y = OH	-830.83764	-830.76816	-830.81104	-830.73551	-830.69773
	Y = OMe	-909.43153	-909.36052	-909.40116	-909.32903	-909.28857
	Y = SH	-1476.75853	-1476.67200	-1476.72460	-1476.63373	-1476.64747
	Y = SiH ₃	-1261.73166	-1261.65662	-1261.68738	-1261.62477	-1261.63904
X = BH ₂	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene				
	Y = BH ₂	REARRANGED				
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene				
	Y = Cl	-1202.24183	-1202.15237	-1202.19480	-1202.11619	-1202.13407
	Y = CN	-467.53374	-467.44607	-467.47764	-467.40188	-467.43486
	Y = F	-481.52389	-481.43605	-481.49171	-481.39948	-481.42008
	Y = Me	Degenerate states				
	Y = NH ₂	REARRANGED				
	Y = NMe ₂	REARRANGED				
	Y = NO ₂	REARRANGED				
	Y = OH	Existence of another excitation with charge transfer character				
	Y = OMe	-512.08500	-512.00067	-512.05302	-511.96835	-511.97432
	Y = BF ₂	-1599.58440	-1599.49688	-1599.52100	-1599.45356	-1599.48212
	Y = BH ₂	-1202.23997	-1202.15864	-1202.18144	-1202.11234	-1202.13807
	Y = CF ₃	-1825.55035	-1825.45521	-1825.48309	-1825.41445	-1825.44767
	Y = Cl	-2070.56753	-2070.49192	-2070.51940	-2070.45840	-2070.46024
	Y = CN	-1335.86857	-1335.79011	-1335.81152	-1335.74907	-1335.76447
	Y = F	-1349.86426	-1349.78607	-1349.81749	-1349.75144	-1349.74578
	Y = Me	-1229.99303	-1229.91025	-1229.93952	-1229.87623	-1229.88086
	Y = NH ₂	-1262.08434	-1262.02485	-1262.06097	-1261.99531	-1261.96352
	Y = NMe ₂	-1419.27915	-1419.21259	-1419.24363	-1419.18492	-1419.15480
	Y = NO ₂	-1560.37626	-1560.29053	-1560.31560	-1560.25228	-1560.28165
	Y = OH	-1301.82596	-1301.75814	-1301.78687	-1301.72680	-1301.70390
	Y = OMe	-1380.41824	-1380.34721	-1380.37457	-1380.31674	-1380.29683
	Y = SH	-1947.74538	-1947.68405	-1947.70785	-1947.65470	-1947.63040

	Y = SiH ₃	-1732.73598	-1732.64585	-1732.67265	-1732.60832	-1732.62831
X = CN	Y = BF ₂	-864.86234	-864.78650	-864.81405	-864.75159	-864.77236
	Y = BH ₂	-467.52201	-467.45081	-467.47648	-467.41265	-467.41034
	Y = CF ₃	-1090.82697	-1090.74869	-1090.77696	-1090.71550	-1090.73714
	Y = Cl	-1335.84963	-1335.79493	-1335.82113	-1335.76787	-1335.75372
	Y = CN	-601.13844	-601.07509	-601.09811	-601.04165	-601.05071
	Y = F	-615.14276	-615.08625	-615.11624	-615.05758	-615.04279
	Y = Me	-495.28097	-495.22114	-495.24772	-495.19432	-495.18220
	Y = NMe ₂	-684.57038	-684.53259	-684.56268	-684.51055	-684.44493
	Y = NH ₂	T ₀ ground state				
	Y = NO ₂	-825.64838	-825.57529	-825.60237	-825.54162	-825.55979
	Y = OH	-567.11015	-567.06645	-567.09359	-567.04053	-567.00583
	Y = OMe	-645.70442	-645.65955	-645.68494	-645.63449	-645.59929
	Y = SH	-1213.02633	-1212.99016	-1213.01230	-1212.96679	-1212.92704
X = F	Y = SiH ₃	-998.01801	-997.94696	-997.97269	-997.91756	-997.92463
	Y = BF ₂	-878.90114	-878.80503	-878.82649	-878.75325	-878.78762
	Y = BH ₂	-481.55545	-481.47281	-481.48865	-481.41658	-481.45053
	Y = CF ₃	-1104.86773	-1104.76181	-1104.78970	-1104.71407	-1104.74438
	Y = Cl	-1349.88269	-1349.79342	-1349.82160	-1349.75386	-1349.76265
	Y = CN	-615.17933	-615.09122	-615.11236	-615.04326	-615.05920
	Y = F	-629.17403	-629.08135	-629.11541	-629.04033	-629.05297
	Y = Me	-509.30598	-509.21003	-509.24144	-509.16931	-509.19078
	Y = NH ₂	-541.39654	-541.32306	-541.36246	-541.28850	-541.27501
	Y = NMe ₂	-698.59242	-698.51214	-698.54703	-698.47959	-698.46799
	Y = NO ₂	Not a clear HOMO-to-LUMO excitation				
	Y = OH	-581.13773	-581.05392	-581.08681	-581.01688	-581.01490
	Y = OMe	-659.72987	-659.64315	-659.67475	-659.60716	-659.60805
	Y = SH	-1227.05818	-1226.98155	-1227.00846	-1226.94703	-1226.94209
X = H	Y = SiH ₃	-1012.04590	-1011.94548	-1011.97193	-1011.90124	-1011.93091
	Y = BF ₂	-680.39326	-680.30386	-680.32617	-680.25493	-680.28852
	Y = BH ₂	LUMO primarily localized on the Y substituents				
	Y = CF ₃	-906.35935	-906.26178	-906.29037	-906.21714	-906.24643
	Y = Cl	-1151.37702	-1151.29683	-1151.32448	-1151.26020	-1151.25604
	Y = CN	-416.67229	-416.59062	-416.61296	-416.54566	-416.56138
	Y = F	-430.66647	-430.58516	-430.61650	-430.54741	-430.53986
	Y = Me	-310.79305	-310.70828	-310.73667	-310.67128	-310.67001
	Y = NH ₂	-342.88483	-342.82102	-342.85299	-342.78979	-342.74887
	Y = NMe ₂	-500.07957	-500.00860	-500.03937	-499.97831	-499.94547
	Y = NO ₂	-641.19470	-641.10997	-641.13224	-641.06331	-641.09529
	Y = OH	-382.62961	-382.55720	-382.58975	-382.52333	-382.49212
	Y = OMe	-461.22166	-461.14634	-461.17322	-461.11353	-461.09072
	Y = SH	-1028.55044	-1028.47484	-1028.50549	-1028.44092	-1028.42314
	Y = SiH ₃	-813.53102	-813.43893	-813.46562	-813.39813	-813.41579
X = Me	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene				

	Y = BH ₂	LUMO primarily localized on the Y substituents				
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene				
	Y = Cl	-1229.99324	-1229.90874	-1229.93722	-1229.87277	-1229.88318
	Y = CN	-495.29774	-495.21272	-495.23361	-495.16776	-495.19120
	Y = F	-509.29085	-509.20351	-509.23458	-509.16537	-509.16568
	Y = Me	-389.40790	-389.31765	-389.34841	-389.28066	-389.29617
	Y = NH ₂	-421.50237	-421.43027	-421.46582	-421.39853	-421.38031
	Y = NMe ₂	-578.69759	-578.61918	-578.65408	-578.58826	-578.58508
	Y = NO ₂	Not a clear HOMO-to-LUMO excitation				
	Y = OH	-719.81119	-719.72153	-719.74341	-719.68055	-719.70183
	Y = OMe	-461.25056	-461.17185	-461.20322	-461.13759	-461.12272
	Y = SH	-539.84182	-539.75944	-539.78722	-539.72639	-539.71662
	Y = SiH ₃	-1107.16687	-1107.09370	-1107.11938	-1107.06188	-1107.05331
X = NH ₂	Y = BF ₂	REARRANGED				
	Y = BH ₂	REARRANGED				
	Y = CF ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
	Y = Cl	-1262.12506	-1262.01607	-1262.04202	-1261.98048	-1261.98881
	Y = CN					
	Y = F	-541.41743	-541.30693	-541.33670	-541.27022	-541.27555
	Y = Me	-421.52981	-421.42265	-421.44698	-421.38583	-421.39771
	Y = NH ₂	T ₁ excitation is different to that of the parent fulvene				
	Y = NMe ₂	Not a clear HOMO-to-LUMO excitation				
	Y = NO ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
	Y = OH	Not a clear HOMO-to-LUMO excitation				
	Y = OMe	Not a clear HOMO-to-LUMO excitation				
	Y = SH	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
	Y = SiH ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
X = NMe ₂	Y = BF ₂	REARRANGED				
	Y = BH ₂	REARRANGED				
	Y = CF ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
	Y = Cl	-1419.31419	-1419.20666	-1419.23321	-1419.17903	-1419.18704
	Y = CN	LUMO primarily localized on the Y substituents				
	Y = F	-698.60304	-698.49494	-698.52455	-698.46356	-698.47096
	Y = Me	-578.71613	-578.61403	-578.64368	-578.58469	-578.59987
	Y = NH ₂	-610.80961	-610.72258	-610.76435	-610.69805	-610.66489
	Y = NMe ₂	-768.00926	-767.91536	-767.94729	-767.89154	-767.88514
	Y = NO ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
	Y = OH	T ₁ excitation is different to that of the parent fulvene				
	Y = OMe	T ₁ excitation is different to that of the parent fulvene				
	Y = SH	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
	Y = SiH ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene				
X = NO ₂	Y = BF ₂	-1089.38110	-1089.30339	-1089.35648	-1089.26854	-1089.26797
	Y = BH ₂	REARRANGED				
	Y = CF ₃	-1315.33487	-1315.25244	-1315.28710	-1315.21654	-1315.24540

	Y = Cl	-1560.35805	-1560.29554	-1560.32911	-1560.26655	-1560.26331
	Y = CN	-825.64763	-825.57923	-825.60515	-825.54310	-825.55155
	Y = F	-839.65194	-839.58934	-839.62503	-839.55937	-839.54709
	Y = Me	-719.78958	-719.72417	-719.75834	-719.69636	-719.69132
	Y = NH ₂	Not a clear HOMO-to-LUMO excitation				
	Y = NMe ₂	-909.07684	-909.01616	-909.07324	-908.99111	-908.96940
	Y = NO ₂	-1050.16616	-1050.08901	-1050.11879	-1050.05265	-1050.08007
	Y = OH	-791.61972	-791.56703	-791.60355	-791.53991	-791.51479
	Y = OMe	-870.21378	-870.16012	-870.19535	-870.13419	-870.10868
	Y = SH	-1437.53764	-1437.48248	-1437.52098	-1437.45701	-1437.43392
	Y = SiH ₃	-1222.52954	-1222.45595	-1222.48633	-1222.42615	-1222.42827
X = OH	Y = BF ₂	Both T1 and S1 excitations are different to that of the parent fulvene				
	Y = BH ₂	Both T1 and S1 excitations are different to that of the parent fulvene				
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene				
	Y = Cl	-1301.84726	-1301.75558	-1301.78272	-1301.71789	-1301.71861
	Y = CN	LUMO primarily localized on the Y substituents				
	Y = F	-581.13922	-581.04478	-581.07595	-581.00584	-581.00448
	Y = Me	-461.26637	-461.16957	-461.19848	-461.13070	-461.13820
	Y = NH ₂	-493.35983	-493.28708	-493.32082	-493.25443	-493.23118
	Y = NMe ₂	HOMO is of a different character compared to that of the parent fulvene				
	Y = NO ₂	REARRANGED				
	Y = OH	-533.11923	-533.02052	-533.04791	-532.98378	-532.97752
	Y = OMe	-611.68979	-611.60113	-611.63540	-611.56695	-611.57049
	Y = SH	-1179.02369	-1178.94417	-1178.96942	-1178.91106	-1178.89395
	Y = SiH ₃	LUMO primarily localized on the Y substituents				
Y=H	Y = BF ₂	-680.37725	-680.30703	-680.33567	-680.27608	-680.27184
	Y = BH ₂	-283.02474	-282.95564	-282.98574	-282.92779	-282.92922
	Y = CF ₃	-906.34182	-906.26261	-906.29250	-906.22680	-906.22808
	Y = Cl	-1151.37446	-1151.28553	-1151.31568	-1151.24810	-1151.26662
	Y = CN	-416.65755	-416.58752	-416.61568	-416.55682	-416.56493
	Y = F	-430.68265	-430.58013	-430.61154	-430.53584	-430.57065
	Y = Me	-310.79405	-310.69687	-310.72617	-310.65615	-310.67989
	Y = NH ₂	Both T1 and S1 excitations are different to that of the parent fulvene				
	Y = NMe ₂	T ₁ excitation is different to that of the parent fulvene				
	Y = NO ₂	-641.17081	-641.09862	-641.12914	-641.06776	-641.06431
	Y = OH	-382.64517	-382.54219	-382.57160	-382.50037	-382.52277
	Y = OMe	-461.23032	-461.11891	-461.15732	-461.07799	-461.10939
	Y = SH	-1028.55370	-1028.46405	-1028.49364	-1028.42856	-1028.44891
	Y = SiH ₃	-813.52405	-813.43957	-813.47039	-813.40391	-813.41739
X=SH	Y = BF ₂	Both T1 and S1 excitations are different to that of the parent fulvene				
	Y = BH ₂	Both T1 and S1 excitations are different to that of the parent fulvene				
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene				
	Y = Cl	-1947.75175	-1947.67019	-1947.69975	-1947.63899	-1947.65157
	Y = CN	T ₁ excitation is different to that of the parent fulvene				

	Y = F	-1227.05024	-1226.96480	-1226.99669	-1226.93150	-1226.93471
	Y = Me	-1107.16914	-1107.08478	-1107.11766	-1107.05310	-1107.06677
	Y = NH ₂	-1139.26652	-1139.19132	-1139.24241	-1139.16146	-1139.14409
	Y = NMe ₂	Not a clear HOMO-to-LUMO excitation				
	Y = NO ₂	-1437.56571	-1437.48873	-1437.50410	-1437.44380	-1437.45850
	Y = OH	-1179.01264	-1178.93577	-1178.96509	-1178.90544	-1178.89706
	Y = OMe	-1257.60491	-1257.52472	-1257.55282	-1257.49516	-1257.49110
	Y = SH	-1824.92542	-1824.85894	-1824.88693	-1824.83209	-1824.82397
	Y = SiH ₃	LUMO is of a different character compared to that of the parent fulvene				
X=CF ₃	Y = BF ₂	-1354.54309	-1354.46208	-1354.49439	-1354.42301	-1354.43915
	Y = BH ₂	-957.20556	-957.12827	-957.15598	-957.08677	-957.08581
	Y = CF ₃	-1580.49995	-1580.41698	-1580.45121	-1580.37898	-1580.42825
	Y = Cl	-1825.52557	-1825.46380	-1825.49461	-1825.43377	-1825.43037
	Y = CN	-1090.82082	-1090.75092	-1090.77602	-1090.71274	-1090.72300
	Y = F	-1104.82474	-1104.75981	-1104.79304	-1104.72726	-1104.71417
	Y = Me	-984.95262	-984.88623	-984.91801	-984.85592	-984.85141
	Y = NH ₂	T ₀ ground state				
	Y = NMe ₂	-1174.23422	-1174.18045	-1174.22610	-1174.15570	-1174.13409
	Y = NO ₂	-1315.33675	-1315.25647	-1315.28600	-1315.21745	-1315.24720
	Y = OH	-1056.78769	-1056.73463	-1056.76673	-1056.70574	-1056.67780
	Y = OMe	-1135.38090	-1135.32668	-1135.35673	-1135.29899	-1135.27070
	Y = SH	-1702.70307	-1702.64425	-1702.68058	-1702.61545	-1702.59987
	Y = SiH ₃	-1487.69297	-1487.61373	-1487.64145	-1487.57913	-1487.58951
X=OMe	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene				
	Y = BH ₂	Not a clear HOMO-to-LUMO excitation				
	Y = CF ₃	Not a clear HOMO-to-LUMO excitation				
	Y = CN	-645.74021	-645.64671	-645.66781	-645.60227	-645.62173
	Y = Cl	-1380.43290	-1380.34290	-1380.37007	-1380.30645	-1380.30768
	Y = F	-659.72907	-659.62668	-659.66224	-659.58931	-659.58800
	Y = Me	-539.85091	-539.75652	-539.78514	-539.71869	-539.72535
	Y = NH ₂	-571.94596	-571.87422	-571.90821	-571.84252	-571.81951
	Y = NMe ₂	-729.13456	-729.04927	-729.08530	-729.01775	-729.01067
	Y = NO ₂	T ₁ excitation is different to that of the parent fulvene				
	Y = OH	Not a clear HOMO-to-LUMO excitation				
	Y = OMe	Not a clear HOMO-to-LUMO excitation				
	Y = SH	-1257.61047	-1257.53218	-1257.55716	-1257.50011	-1257.48323
	Y = SiH ₃	-1042.59837	-1042.49857	-1042.52406	-1042.45713	-1042.48047
X=SiH ₃	Y = BF ₂	-1261.73811	-1261.65200	-1261.67745	-1261.60965	-1261.64999
	Y = BH ₂	REARRANGED				
	Y = CF ₃	-1487.69970	-1487.60910	-1487.63993	-1487.56916	-1487.61003
	Y = CN	-998.02164	-997.94477	-997.96815	-997.90449	-997.92692
	Y = Cl	-1732.72526	-1732.65344	-1732.68253	-1732.62163	-1732.62520
	Y = F	-1012.02126	-1011.94796	-1011.98014	-1011.91512	-1011.90527
	Y = Me	-892.14009	-892.06584	-892.09595	-892.03477	-892.03824

Y = NH ₂	-924.23791	-924.17569	-924.21870	-924.14820	-924.12374
Y = NMe ₂	-1081.43770	-1081.36877	-1081.40155	-1081.34281	-1081.31300
Y = NH ₂	Not a clear HOMO-to-LUMO excitation				
Y = OH	-963.98477	-963.92161	-963.95142	-963.89223	-963.86629
Y = OMe	-1042.57818	-1042.51277	-1042.54106	-1042.48444	-1042.45782
Y = SH	-1609.89753	-1609.81582	-1609.86328	-1609.78105	-1609.79777
Y = SiH ₃	-1394.87748	-1394.79215	-1394.82202	-1394.75711	-1394.77940

Table S5. NICS(1)_{zz} values in the S₀ and T₁ states of the differently substituted fulvenes. For label “REARRANGED” see Table S2.

		NICS(1) _{zz}		HOMA	
		S ₀	T ₁	S ₀	T ₁
X=H	Y = H	-5.6	5.0	-0.33	0.27
X = BF ₂	Y = BF ₂	-2.7	-0.1	-0.39	0.21
	Y = BH ₂	-2.7	-10.9	-0.38	0.34
	Y = CF ₃	-2.4	9.1	-0.46	0.29
	Y = Cl	4.2	-4.2	-0.50	0.49
	Y = CN	-5.2	1.8	-0.20	0.20
	Y = F	10.7	-6.4	-0.66	0.62
	Y = Me	11.6	-8.1	-0.83	0.38
	Y = NH ₂	REARRANGED			
	Y = NMe ₂	REARRANGED			
	Y = NO ₂	REARRANGED			
	Y = OH	9.1	-9.6	-0.52	0.59
	Y = OMe	10.4	-10.0	-0.50	0.55
	Y = SH	-0.6	-11.4	-0.37	0.43
	Y = SiH ₃	5.4	-3.2	-0.83	0.17
X = BH ₂	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene			
	Y = BH ₂	REARRANGED			
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene			
	Y = Cl	-6.5	0.2	-0.03	0.48
	Y = CN	-15.2	7.5	0.25	0.14
	Y = F	-2.1	-4.3	-0.20	0.63
	Y = Me	Degenerate states			
	Y = NH ₂	REARRANGED			
	Y = NMe ₂	REARRANGED			
	Y = NO ₂	REARRANGED			
	Y = OH	Existence of another excitation with charge transfer character			
	Y = OMe	-0.5	-7.7	-0.14	0.54
	Y = SH	REARRANGED			
	Y = SiH ₃	REARRANGED			
X = Cl	Y = BF ₂	-4.6	10.1	-0.08	-0.14
	Y = BH ₂	-8.0	9.1	-0.07	-0.31
	Y = CF ₃	-4.4	15.9	-0.24	0.12
	Y = Cl	-1.3	2.7	-0.44	0.38
	Y = CN	-7.9	9.0	0.05	-0.02
	Y = F	2.0	-0.4	-0.40	0.53
	Y = Me	-1.1	2.5	-0.59	0.26
	Y = NH ₂	3.8	-9.5	-0.66	0.54
	Y = NMe ₂	3.1	-8.4	-0.65	0.42
	Y = NO ₂	-4.3	15.0	0.09	0.23
	Y = OH	3.6	-4.6	-0.48	0.51

	Y = OMe	5.0	-4.2	-0.49	0.46
	Y = SH	-0.8	-3.4	-0.46	0.35
	Y = SiH ₃	-5.7	9.3	-0.31	-0.04
X = CN	Y = BF ₂	2.5	1.7	-0.33	0.17
	Y = BH ₂	0.9	-6.1	-0.36	0.39
	Y = CF ₃	5.4	5.7	-0.47	0.31
	Y = Cl	11.7	-3.5	-0.59	0.49
	Y = CN	1.5	2.6	-0.22	0.21
	Y = F	15.7	-5.0	-0.61	0.65
	Y = Me	13.0	-4.8	-0.75	0.41
	Y = NH ₂	T ₀ ground state			
	Y = NMe ₂	21.5	-10.5	-0.66	0.46
	Y = NO ₂	4.9	3.1	-0.26	0.42
	Y = OH	20.3	-8.6	-0.64	0.62
	Y = OMe	22.7	-9.1	-0.62	0.58
	Y = SH	16.0	-8.1	-0.66	0.49
	Y = SiH ₃	4.5	0.4	-0.59	0.20
X = F	Y = BF ₂	-14.0	15.5	0.18	-0.31
	Y = BH ₂	-13.5	16.2	0.19	-0.50
	Y = CF ₃	-9.8	12.3	0.09	0.08
	Y = Cl	-5.5	1.8	-0.09	0.41
	Y = CN	-12.4	7.9	0.26	-0.07
	Y = F	-3.1	1.7	-0.20	0.59
	Y = Me	-4.9	4.1	-0.24	0.35
	Y = NH ₂	0.9	-9.9	-0.35	0.63
	Y = NMe ₂	0.1	-7.8	-0.34	0.57
	Y = NO ₂	Not a clear HOMO-to-LUMO excitation			
	Y = OH	-1.1	-4.2	-0.22	0.59
	Y = OMe	0.1	-2.2	-0.22	0.54
	Y = SH	-3.9	-4.1	-0.15	0.49
	Y = SiH ₃	-10.7	10.6	-0.04	0.03
X = H	Y = BF ₂	-10.5	14.4	-0.07	-0.20
	Y = BH ₂	LUMO primarily localized on the Y substituents			
	Y = CF ₃	-5.5	10.5	-0.21	0.18
	Y = Cl	1.7	-0.7	-0.38	0.39
	Y = CN	-7.2	6.0	-0.06	0.02
	Y = F	3.3	-2.0	-0.46	0.55
	Y = Me	3.3	-2.0	-0.53	0.29
	Y = NH ₂	10.4	-11.3	-0.59	0.54
	Y = NMe ₂	8.0	-9.3	-0.57	0.38
	Y = NO ₂	-5.6	14.4	-0.05	0.07
	Y = OH	6.2	-8.9	-0.49	0.57
	Y = OMe	7.3	-6.0	-0.47	0.48
	Y = SH	1.6	-6.4	-0.39	0.44

	Y = SiH ₃	-4.8	5.1	-0.39	0.00
X = Me	Y = BF ₂	T ₁ excitation is different to that of the parent fulvene			
	Y = BH ₂	LUMO primarily localized on the Y substituents			
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene			
	Y = Cl	-5.5	6.1	-0.27	0.32
	Y = CN	-12.3	12.6	0.10	-0.12
	Y = F	-1.8	1.9	-0.37	0.49
	Y = Me	-4.9	6.0	-0.51	0.21
	Y = NH ₂	-1.6	-6.6	-0.54	0.52
	Y = NMe ₂	-0.7	-4.0	-0.55	0.39
	Y = NO ₂	Not a clear HOMO-to-LUMO excitation			
	Y = OH	-0.4	-3.7	-0.43	0.51
	Y = OMe	0.1	-1.0	-0.40	0.41
	Y = SH	-5.5	-0.4	-0.33	0.34
	Y = SiH ₃	-10.5	14.3	-0.25	-0.15
X = NH ₂	Y = BF ₂	REARRANGED			
	Y = BH ₂	REARRANGED			
	Y = CF ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
	Y = Cl	-17.7	10.7	0.46	0.19
	Y = CN	LUMO primarily localized on the Y substituents			
	Y = F	-15.0	7.7	0.36	0.42
	Y = Me	-15.6	8.6	0.22	0.19
	Y = NH ₂	T ₁ excitation is different to that of the parent fulvene			
	Y = NMe ₂	Not a clear HOMO-to-LUMO excitation			
	Y = NO ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
	Y = OH	Not a clear HOMO-to-LUMO excitation			
	Y = OMe	Not a clear HOMO-to-LUMO excitation			
	Y = SH	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
	Y = SiH ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
X = NMe ₂	Y = BF ₂	REARRANGED			
	Y = BH ₂	REARRANGED			
	Y = CF ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
	Y = Cl	-18.9	13.2	0.64	0.26
	Y = CN	LUMO primarily localized on the Y substituents			
	Y = F	-15.9	9.0	0.42	0.45
	Y = Me	-17.0	11.6	0.36	0.20
	Y = NH ₂	-11.1	-9.2	0.26	0.52
	Y = NMe ₂	-13.5	-2.1	0.35	0.37
	Y = NO ₂	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
	Y = OH	T ₁ excitation is different to that of the parent fulvene			
	Y = OMe	T ₁ excitation is different to that of the parent fulvene			
	Y = SH	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
	Y = SiH ₃	Both T ₁ and S ₁ excitations are different to that of the parent fulvene			
X = NO ₂	Y = BF ₂	3.2	-18.3	-0.49	0.66

	Y = BH ₂		REARRANGED	
	Y = CF ₃	3.6	2.0	-0.61 0.38
	Y = Cl	10.8	-7.2	-0.65 0.54
	Y = CN	2.8	-3.2	-0.37 0.24
	Y = F	14.2	-8.4	-0.72 0.66
	Y = Me	14.5	-9.7	-0.87 0.45
	Y = NH ₂		Not a clear HOMO-to-LUMO excitation	
	Y = NMe ₂	8.3	-10.9	-0.64 0.36
	Y = NO ₂	5.2	2.4	-0.37 0.45
	Y = OH	17.3	-10.9	-0.70 0.63
	Y = OMe	19.5	-11.3	-0.68 0.59
	Y = SH	11.1	-12.3	-0.71 0.45
	Y = SiH ₃	6.6	-7.6	-0.79 0.26
X = OH	Y = BF ₂	Both T1 and S1 excitations are different to that of the parent fulvene		
	Y = BH ₂	Both T1 and S1 excitations are different to that of the parent fulvene		
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene		
	Y = Cl	-8.3	3.8	0.04 0.29
	Y = CN	LUMO primarily localized on the Y substituents		
	Y = F	-5.7	1.5	-0.06 0.48
	Y = Me	-7.2	3.9	-0.14 0.19
	Y = NH ₂	-0.1	-8.1	-0.30 0.60
	Y = NMe ₂	HOMO is of a different character compared to that of the parent fulvene		
	Y = NO ₂	REARRANGED		
	Y = OH	-9.6	0.5	0.15 0.49
	Y = OMe	-2.4	2.3	-0.13 0.42
	Y = SH	-7.1	-2.1	-0.01 0.35
	Y = SiH ₃	LUMO primarily localized on the Y substituents		
Y=H	Y = BF ₂	8.8	-5.8	-0.75 0.42
	Y = BH ₂	6.2	-2.8	-0.64 0.45
	Y = CF ₃	5.6	-4.0	-0.70 0.38
	Y = Cl	-1.7	5.7	-0.21 0.31
	Y = CN	9.2	-1.4	-0.47 0.47
	Y = F	-9.7	9.1	-0.03 0.32
	Y = Me	-8.0	9.0	-0.18 0.22
	Y = NH ₂	Both T1 and S1 excitations are different to that of the parent fulvene		
	Y = NMe ₂	T ₁ excitation is different to that of the parent fulvene		
	Y = NO ₂	9.3	-8.3	-0.65 0.47
	Y = OH	-11.4	9.1	0.10 0.20
	Y = OMe	-18.0	9.8	0.28 0.21
	Y = SH	-4.9	8.2	-0.13 0.31
	Y = SiH ₃	-0.8	1.5	-0.53 0.33
X=SH	Y = BF ₂	Both T1 and S1 excitations are different to that of the parent fulvene		
	Y = BH ₂	Both T1 and S1 excitations are different to that of the parent fulvene		
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene		

	Y = Cl	-6.9	6.4	-0.10	0.40
	Y = CN	T ₁ excitation is different to that of the parent fulvene			
	Y = F	-4.4	2.7	-0.12	0.53
	Y = Me	-4.5	3.8	-0.40	0.30
	Y = NH ₂	-4.8	-10.8	-0.23	0.50
	Y = NMe ₂	Not a clear HOMO-to-LUMO excitation			
	Y = NO ₂	-14.0	22.0	0.43	0.43
	Y = OH	-3.5	-0.7	-0.18	0.53
	Y = OMe	-2.3	1.1	-0.19	0.48
	Y = SH	-3.6	-3.3	-0.20	0.41
	Y = SiH ₃	LUMO is of a different character compared to that of the parent fulvene			
X=CF ₃	Y = BF ₂	2.3	-0.7	-0.68	0.13
	Y = BH ₂	1.6	-6.7	-0.63	0.18
	Y = CF ₃	3.5	14.1	-0.88	0.32
	Y = Cl	11.3	-3.2	-0.80	0.47
	Y = CN	2.2	0.9	-0.50	0.14
	Y = F	13.5	-5.4	-0.78	0.61
	Y = Me	14.7	-5.7	-1.06	0.35
	Y = NH ₂	T ₀ ground state			
	Y = NMe ₂	14.6	-9.7	-0.89	0.43
	Y = NO ₂	2.9	7.2	-0.50	0.35
	Y = OH	17.5	-8.5	-0.83	0.59
	Y = OMe	19.9	-9.0	-0.80	0.55
	Y = SH	10.6	-9.4	-0.90	0.45
	Y = SiH ₃	5.1	-1.6	-0.99	0.09
X=OMe	Y = BF ₂	LUMO primarily localized on the Y substituents			
	Y = BH ₂	HOMO and LUMO primarily localized on the Y substituents			
	Y = CF ₃	T ₁ excitation is different to that of the parent fulvene			
	Y = CN	-17.3	12.6	0.55	-0.09
	Y = Cl	-7.2	4.2	0.04	0.30
	Y = F	-11.0	1.3	0.16	0.49
	Y = Me	-5.8	3.8	-0.17	0.20
	Y = NH ₂	1.0	-7.9	-0.31	0.59
	Y = NMe ₂	-4.0	-5.3	-0.20	0.43
	Y = NO ₂	T ₁ excitation is different to that of the parent fulvene			
	Y = OH	Not a clear HOMO-to-LUMO excitation			
	Y = OMe	Not a clear HOMO-to-LUMO excitation			
	Y = SH	-5.7	-2.0	-0.01	0.36
	Y = SiH ₃	-12.3	12.4	0.11	-0.08
X=SiH ₃	Y = BF ₂	-5.3	15.1	-0.36	-0.12
	Y = BH ₂	REARRANGED			
	Y = CF ₃	-2.7	15.0	-0.59	0.12
	Y = CN	3.5	-0.2	-0.24	0.02
	Y = Cl	-6.8	8.7	-0.62	0.40

Y = F	2.2	1.7	-0.60	0.58
Y = Me	5.2	-1.5	-0.86	0.29
Y = NH ₂	5.9	-9.8	-0.69	0.52
Y = NMe ₂	5.0	-7.9	-0.58	0.38
Y = NO ₂	Not a clear HOMO-to-LUMO excitation			
Y = OH	6.6	-5.4	-0.65	0.56
Y = OMe	8.2	-5.4	-0.62	0.51
Y = SH	-0.7	-4.3	-0.55	0.43
Y = SiH ₃	-3.2	6.4	-0.73	-0.02

Table S6. MCI values for ten fulvenes at TD-M06-2X/def2-TZVPD level.

MCI	S ₀	T ₁	S ₁
X = BF ₂ Y = OH	0.006	0.012	0.014
X = NO ₂ Y = F	0.004	0.013	0.015
X = CN Y = Cl	0.006	0.016	0.019
X = NO ₂ Y = Cl	0.005	0.015	0.018
X = BF ₂ Y = OMe	0.006	0.012	0.014
X = BF ₂ Y = F	0.006	0.012	0.014
X = CF ₃ Y = Cl	0.005	0.014	0.017
X = NO ₂ Y = Me	0.002	0.016	0.018
X = CF ₃ Y = F	0.005	0.013	0.014
X = H Y = NH ₂	0.006	0.013	0.016

The cyclopentadienyl cation (Cp⁺) in its lowest singlet and triplet states represent references for, respectively, Hückel-antiaromaticity (MCI = -0.034) and Baird-aromaticity (MCI = 0.097). The cyclopentadienyl anion (Cp⁻) in its lowest singlet and triplet states is Hückel-aromatic (MCI = 0.068) and Baird-antiaromatic (MCI = 0.026), respectively. When analyzing MCI, it is better to investigate the differences, *i.e.* ΔMCI(T₁-S₀). In case of Cp⁺ such difference is highly positive (0.131) indicating that the molecules gains aromaticity from the S₀ to the T₁ state. On the other hand, for Cp⁻ the difference is negative (-0.042) revealing loss of aromaticity. Also, it is worth mentioning that Cp⁺ in the triplet state has a higher MCI (0.097) compared to Cp⁻ and that is indicative that Cp⁺ is more Baird-aromatic than Cp⁻.

Note on Cartesian coordinates: The coordinates of the optimized geometries of the substituted fulvenes, listed in Tables S2-S6, in their S₀ and T₁ states are available upon request from the authors.

Table S7. Electronic excitation energies (eV) of the selected tetrasubstituted fulvenes at TD-M06-2X/def2-TZVPD and CASPT2(14in14)/ANO-RCC-VDZP (in italics)^a levels.

Fulvene	$E(T_1)_a^b$	$E(S_1)_v^c$	$E(T_2)^d$	$E(S_1)_v/E(T_1)_a$	$E(T_2)/E(S_1)_v$	$E(T_2)/E(T_1)_a$
X = CN, Y = NMe ₂	0.21, <i>0.56</i>	1.63, <i>2.04</i>	3.41, <i>3.28</i>	7.76, <i>3.64</i>	2.09, <i>1.61</i>	16.24, <i>5.86</i>
X = NO ₂ , Y = NH ₂	0.28, <i>0.21</i>	1.68, <i>1.52</i>	3.21, <i>3.32</i>	6.00, <i>7.24</i>	1.91, <i>2.18</i>	11.46, <i>15.78</i>
X = CF ₃ , Y = NMe ₂	0.46, <i>0.66</i>	2.18, <i>2.55</i>	2.89, <i>3.17</i>	4.74, <i>3.86</i>	1.33, <i>1.24</i>	6.28, <i>4.79</i>
X = CN, Y = OMe	0.53, <i>0.61</i>	1.90, <i>2.26</i>	2.86, <i>3.13</i>	3.58, <i>3.70</i>	1.51, <i>1.38</i>	5.40, <i>5.11</i>
X = CN, Y = F	0.72, <i>0.93</i>	2.32, <i>2.66</i>	2.72, <i>3.07</i>	3.22, <i>2.86</i>	1.17, <i>1.15</i>	3.78, <i>3.29</i>
X = BF ₂ , Y = F	0.83, <i>0.77</i>	2.74, <i>3.04</i>	2.90, <i>2.96</i>	3.30, <i>3.95</i>	1.06, <i>0.97</i>	3.49, <i>3.83</i>
X = OMe, Y = NH ₂	1.03, <i>1.26</i>	2.81, <i>3.10</i>	3.44, <i>3.62</i>	2.73, <i>2.46</i>	1.22, <i>1.17</i>	3.34, <i>2.88</i>
X = CN, Y = SiH ₃	1.23, <i>1.25</i>	2.73, <i>3.04</i>	2.54, <i>2.75</i>	2.22, <i>2.43</i>	0.93, <i>0.90</i>	2.07, <i>2.19</i>

^a The active space includes five occupied valence π -orbitals, the two highest occupied σ -orbitals and the corresponding virtual ones. In case that the compound has only three occupied valence π -orbitals, the four highest occupied σ -orbitals are taken.

^b Adiabatic triplet M06-2X/def2-TZVPD excitation energies computed at M06-2X/6-311+G(d,p) triplet optimized geometry.

^c First singlet TD-M062X/def2-TZVPD vertical excitations computed from the M06-2X/6-311+G(d,p) ground state optimized structure.

^d Second triplet TD-M062X/def2-TZVPD vertical excitations computed from the M06-2X/6-311+G(d,p) lowest triplet optimized structure.

Table S8. Comparison of experimental $E(S_1)$ and $E(T_1)$ and computed $E(S_1)$, $E(T_1)_v$ and adiabatic $E(T_1)_a$ of a DPB, pentacene, tetracene and four fulvenes. Corresponding ratios $E(S_1)/E(T_1)$ are also provided. Energies computed at TD-M06-2X/def2-TZVPD level except the ones in parenthesis which are computed at CASPT2/ANO-RCC-VDZP// TD-M06-2X/def2-TZVPD level.

	$E(S_1)_{\text{exp}}$	$E(S_1)_v$	$E(T_1)_{\text{exp}}$	$E(T_1)_v$	$E(T_1)_a$	$E(S_1)_{\text{exp}}/E(T_1)_{\text{exp}}$	$E(S_1)_v/E(T_1)_v$	$E(S_1)_v/E(T_1)_a$
DPB	3.22	3.01	1.41	2.11	1.64	2.13	1.53	1.96
pentacene	2.30	2.28	0.86	1.33	0.98	2.67	1.72	2.33
tetracene	2.32	2.83	1.25	1.57	1.44	1.86	1.80	1.97
TCIDMF	3.48	3.29	1.98	2.40	1.58	1.76	1.37	2.08
TCIDPF	3.62	3.46	2.17	2.76	2.09	1.67	1.26	1.66
6,6-DMF*	3.50	3.75	1.98	2.64	1.85	1.76	1.42	2.02
T ^t BuEDCF	-	1.74	-	1.02	0.64	-	1.71	2.72
NDPDCF	-	2.05	-	1.51	0.94	-	1.36	2.18
PDPDCF	-	1.84	-	1.23	0.69	-	1.50	2.67
DMDPDCF	-	2.23	-	1.57 (1.95)	0.92	-	1.42	2.42
DCIDPDCF	-	2.38	-	1.70 (2.26)	0.96	-	1.40	2.48
TCIDCF	2.29	2.48	< 1.18	1.67 (2.16)	0.82	-	1.49	3.02

* 6,6-DMF = 6,6-dimethylfulvene

Spin-orbit coupling calculations

As the T_1 excitons formed in an efficient singlet fission chromophore should be long-lived, we investigated the probability for spin-forbidden T_1/S_0 state processes such as intersystem crossing and phosphorescence in fulvenes. If a triplet exciton is close to a T_1/S_0 crossing point with high spin-orbit coupling (SOC), leading to rapid decay to the S_0 state, the efficiency will be hampered. However, the SOC elements for T_1/S_0 in our eight fulvenes computed at TD-M06-2X level range from 0.4 to 2.8 cm^{-1} (Table S9) which is typical of weak couplings and indicating that intersystem crossing will not impede the singlet fission process.

Table S9. Spin-orbit coupling ($\langle T_1 | H | S_0 \rangle$) elements (in cm^{-1}) and %TAE([T]) values computed at CCSD(T)/aug-cc-pVDZ level for a small selection of fulvenes.

System	$\langle T_1 H S_0 \rangle$	%TAE([T])
X = CN Y = NMe ₂	1.0	3.145
X = NO ₂ Y = NH ₂	1.1	3.216
X = CF ₃ Y = NMe ₂	1.8	2.516 ^a
X = CN Y = OMe	0.3	2.831
X = NO ₂ Y = BF ₂	1.3	2.738
X = CN Y = F	0.4	3.766
X = BF ₂ Y = F	1.7	2.613
X = OMe Y = NH ₂	1.7	2.964
X = CN Y = SiH ₃	0.4	4.105
X = CN Y = BF ₂	2.8	3.629
X = BF ₂ Y = CF ₃	0.5	3.235 ^a
X = BF ₂ Y = NO ₂	0.4	1.968
X = NH ₂ Y = NMe ₂	1.9	2.624 ^a

^a Computed at CCSD(T)/cc-pVDZ due to memory issues

Assessment of the multiconfigurational character in fulvenes

Excitation energies calculated with TDDFT are reliable only if there is no evidence of multiconfigurational character, at least at the geometry in the S_0 state. To probe for multiconfigurational character, we used the %TAE_e[(T)], *i.e.*, the percentage of the perturbative triples correction (T) to the total CCSD(T) atomization energy, proposed by Karton *et al.*⁵⁶ The computed %TAE_e[(T)] values for the S_0 states of the fulvenes in Figure 5 are found in the range 2.0 - 4.1 % (Table S9), indicating lack of multiconfigurational character as the values are below the recommended threshold of 10%.⁴

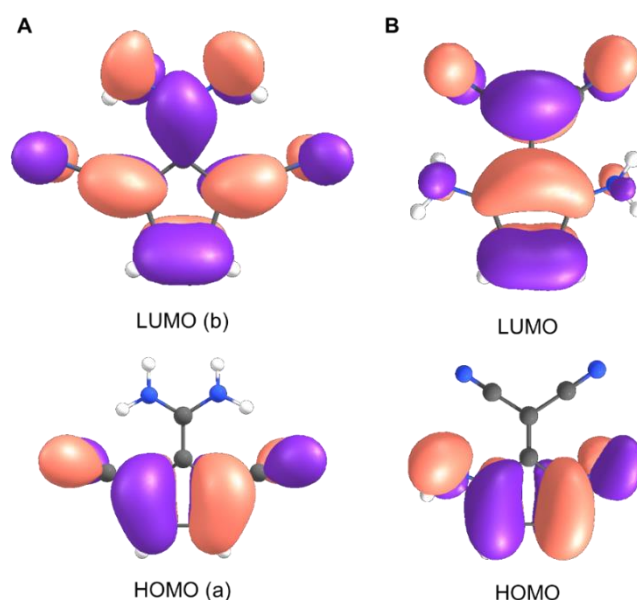


Figure S1: Plots of HOMO and LUMO of (A) the fulvene with X = CN and Y = NH₂, and (B) the fulvene with X = NH₂ and Y = CN. Calculated for the S_0 state at M06-2X/6-311+G(d,p) level.

Calculation of the diradical character

The diradical character was computed using the spin-projected spin-unrestricted Hartree-Fock (PUHF) proposed by Yamaguchi^{S7} given by,

$$y_n = 1 - \frac{2T_n}{1 + T_n^2}$$

where T_n is the orbital overlap between the corresponding orbital pairs than can be also expressed in the terms of natural occupation numbers, η , of UHF natural orbitals as,

$$T_n = \frac{\eta_{HOMO-n} - \eta_{LUMO+n}}{2}$$

Diradical ($n=0$) and tetraradical ($n=1$) characters have been calculated (Table S10).

Table S10. Diradical (y_0) and tetraradical (y_1) character.

	y_0	y_1
Fulvenes		
X = Cl Y = NH ₂	0.037	0.001
X = CN Y = SH	0.077	0.002
X = CN Y = OH	0.052	0.002
X = CN Y = NH ₂	0.087	0.002
X = CN Y = OMe	0.047	0.001
X = CF ₃ Y = OH	0.045	0.002
X = CF ₃ Y = SH	0.057	0.002
X = CN Y = NMe ₂	0.059	0.002
X = CF ₃ Y = NMe ₂	0.043	0.001
X = NO ₂ Y = SH	0.061	0.002
X = NO ₂ Y = OMe	0.040	0.001
X = CF ₃ Y = NH ₂	0.073	0.002
X = NO ₂ Y = NMe ₂	0.038	0.001
TCIDCF(H ₂) ²⁺	0.129	0.002
CBD	0.191	0.004
parent pentalene	0.259	0.006
Cyclopentadienyl cation	0.956	0.003
Substituted CBDs		
SCBD1	0.189	0.004
SCBD2	0.244	0.005
SCBD3	0.192	0.004
SCBD4	0.151	0.003
Benzannelated CBDs		
BENZCBD1	0.109	0.009
BENZCBD2	0.226	0.023
BENZCBD5	0.281	0.036
Benzannelated pentalenes		
BENZPENT1	0.179	0.016
BENZPENT3	0.261	0.030
BENZPENT4	0.264	0.030
BENZPENT6	0.479	0.020
BENZPENT7	0.299	0.034
BENZPENT11	0.598	0.043
BENZPENT19	0.011	0.000

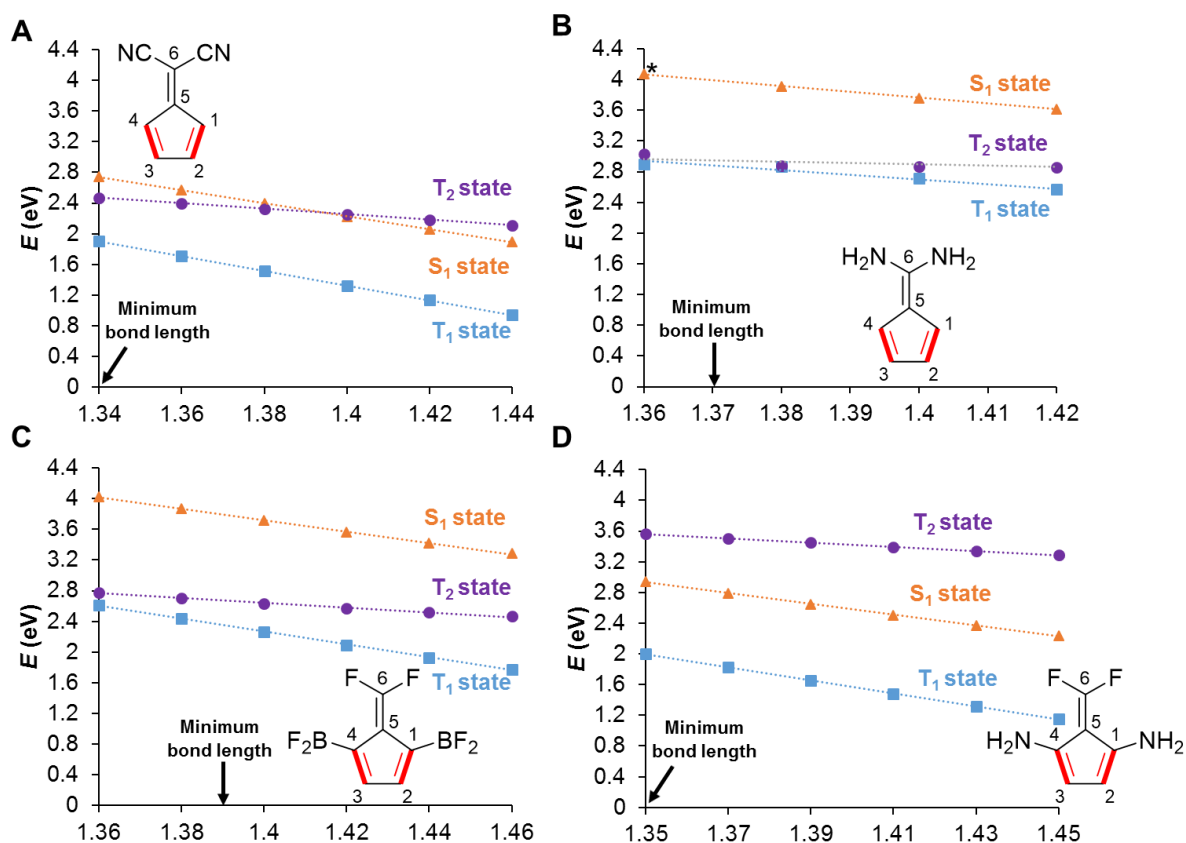


Figure S2. Two plots showing how $E(T_1)_v$, $E(S_1)_v$ and $E(T_2)$ vary as functions of the CC bond lengths marked in red of four fulvenes, (A) $X = \text{CN}$, $Y = \text{H}$, (B) $X = \text{NH}_2$, $Y = \text{H}$, (C) $X = \text{F}$, $Y = \text{BF}_2$ and (D) $X = \text{F}$, $Y = \text{NH}_2$. Calculations at TD-M06-2X/6-311+G(d,p) level.

Table S11. The $\Delta E(S_1-T_1)$ of the parent fulvene and substituted fulvenes in Figure 2 and Figure S2.

$\Delta E(S_1-T_1)$	C2-C3 bond	C1-C2/C3-C4
$X = \text{H}$	1.00 – 1.13	1.04 – 1.16
$X = \text{CN}$	0.83 – 0.86	0.84 – 0.96
$X = \text{NH}_2$	1.04 – 1.48*	1.04 – 1.17
$X = \text{F}$, $Y = \text{BF}_2$	1.40 – 1.49	1.41 – 1.51
$X = \text{F}$, $Y = \text{NH}_2$	0.92 – 0.98	0.94 – 1.08

* The S_1 and T_1 excitations of this fulvene is not described by the same configurations, *i.e.* the singly excited configuration involving the proper HOMO and LUMO.

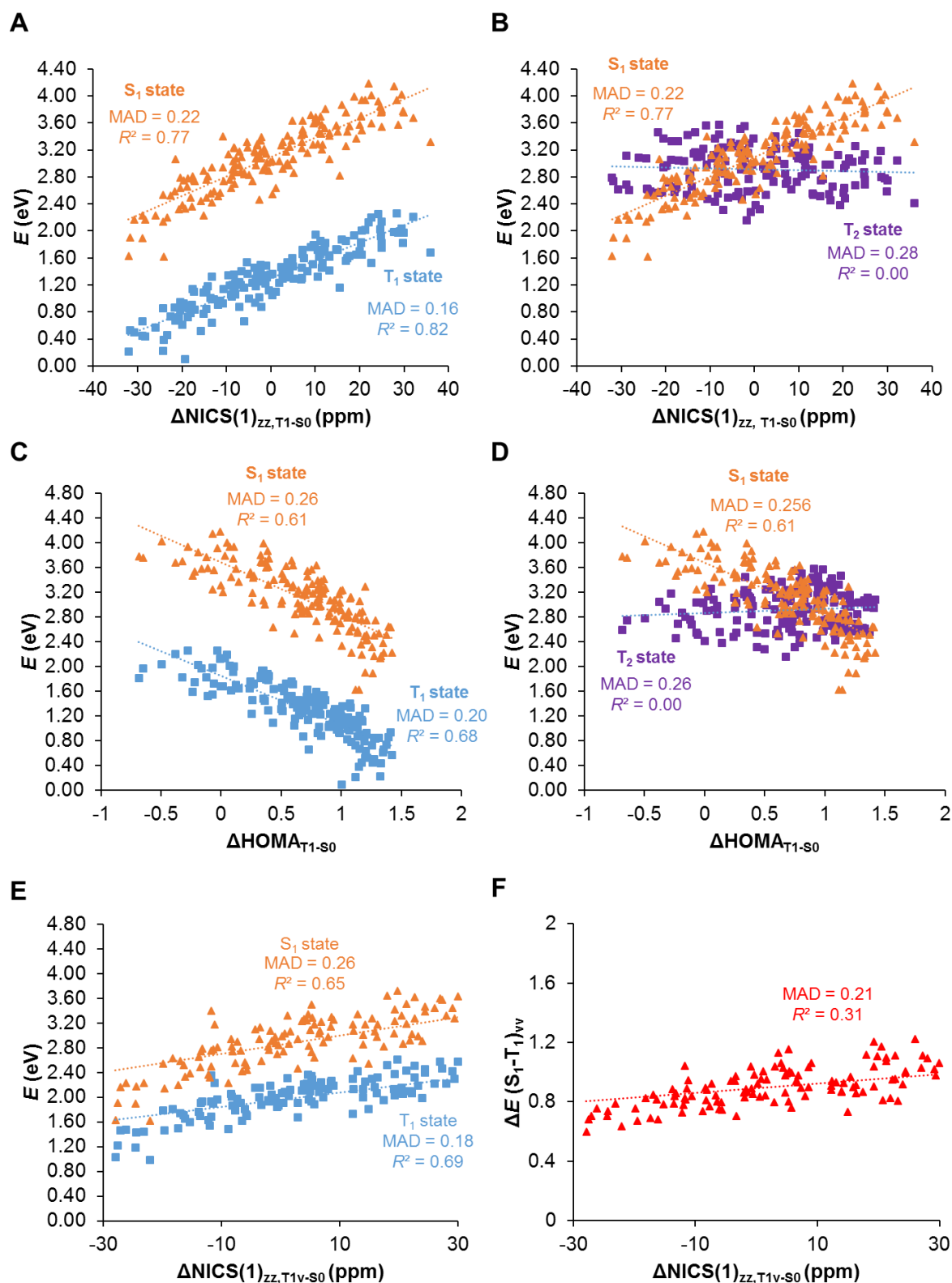


Figure S3: (A) The $E(S_1)_v$ and $E(T_1)_a$ plotted vs. $\Delta NICS(1)_{zz,T1-S0}$, (B) $E(T_2)$ and $E(S_1)_v$ plotted vs. $\Delta NICS(1)_{zz,T1-S0}$, (C) the $E(S_1)_v$ and $E(T_1)_a$ plotted vs. $\Delta HOMA_{T1-S0}$, (D) $E(T_2)$ and $E(S_1)_v$ plotted vs. $\Delta HOMA_{T1-S0}$, (E) the $E(S_1)_v$ and $E(T_1)_v$ plotted vs. $\Delta NICS(1)_{zz,T1v-S0}$, and (F) $\Delta E(S_1-T_1)_{vv}$ plotted vs. $\Delta NICS(1)_{zz,T1v-S0}$ calculated at GIAO/(U)M06-2X/6-311+G(d,p) level.

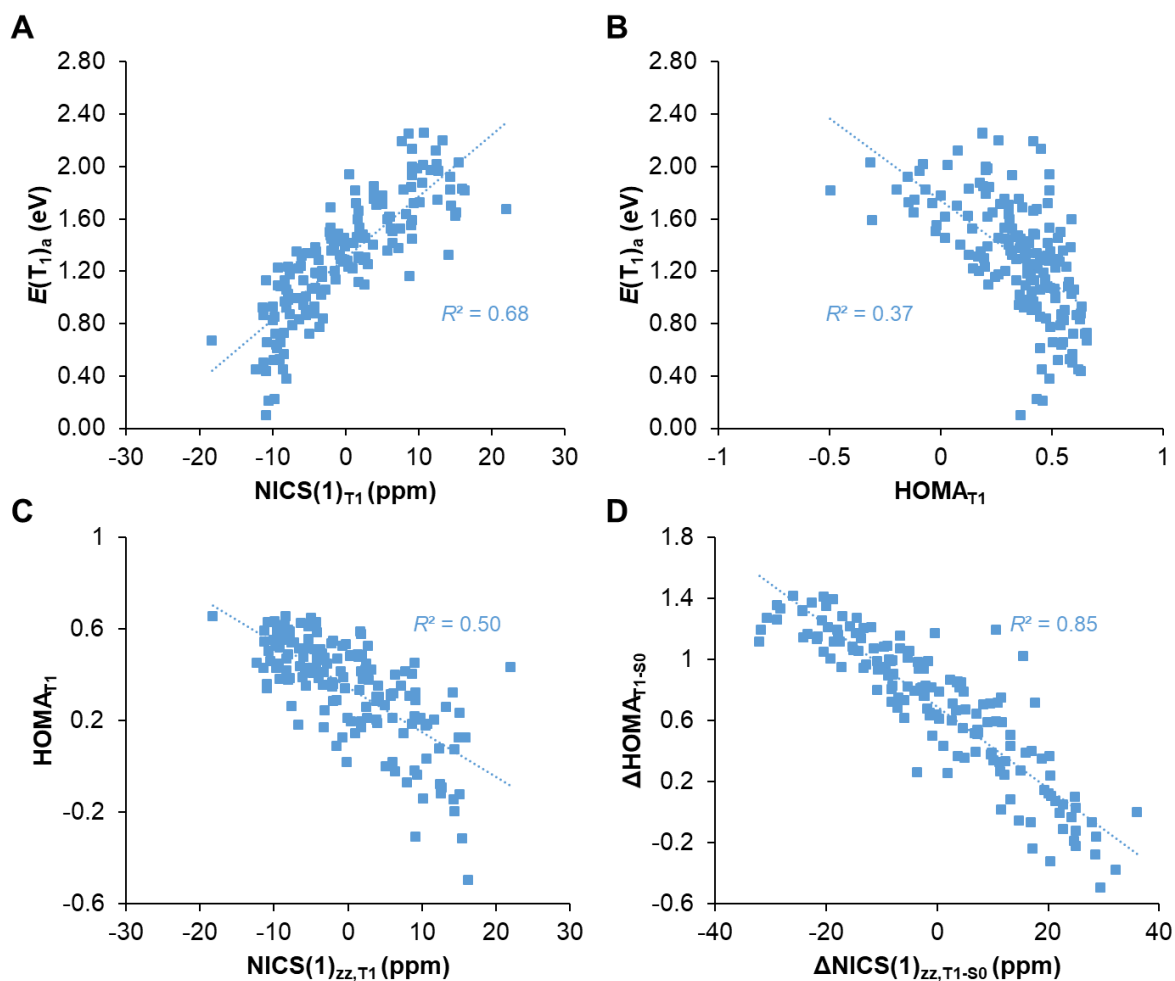


Figure S4: The $E(T_1)_a$ plotted vs. (A) $\text{NICS}(1)_{T1}$ and (B) HOMA_{T1} , (C) HOMA_{T1} vs. $\text{NICS}(1)_{T1}$ and (D) $\Delta\text{HOMA}_{T1-S0}$ vs. $\Delta\text{NICS}(1)_{T1-S0}$ calculated at GIAO/(U)M06-2X/6-311+G(d,p) level.

The poorer correlation of plot B when compared to plot A comes from the fact that HOMA is not ideal to describe the T_1 aromaticity of molecules with small four- and five-membered rings. A clear example is cyclopentadienyl cation (Cp^+), a Baird-aromatic reference, which has an HOMA value (0.73), significantly below the ideal aromatic HOMA value of 1.0.

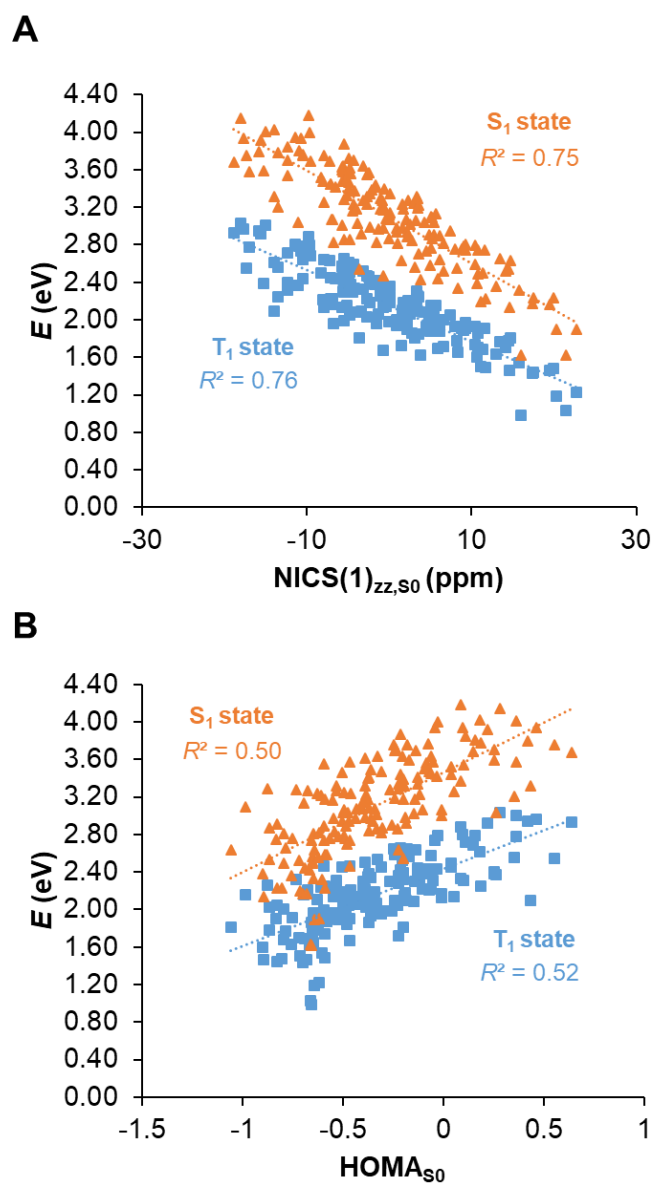


Figure S5. A comparison of the dependence of $E(S_1)_v$ and $E(T_1)_v$ on (A) $NICS(1)_{zz,S0}$ and (B) $HOMA_{S0}$ of fulvenes. R^2 is the squared correlation coefficient. Calculations at M06-2X/6-311+G(d,p).

SUBSTITUTED CBDs

Weights of the singly excited HOMO to LUMO configurations of substituted CBDs
In all cases the major configuration in the S_1 state is the HOMO to LUMO transition.

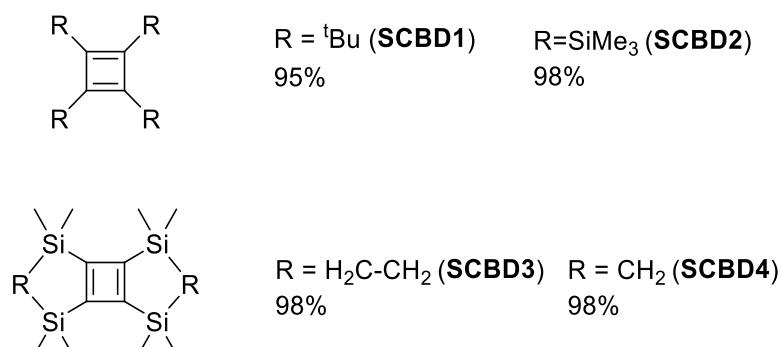


Figure S6. Percentage of the singly excited HOMO to LUMO configuration in the S_1 state of CBD and substituted CBDs (SCBD)s.

Table S12. Coefficients of the major configurations from Gaussian output of the CBD derivatives.

SCBD1	Excited State 1: Singlet-A	2.5628 eV	483.78 nm	f=0.0001	<S**2>=0.000
	78 -> 79	0.69126			
	78 -> 80	-0.11739			
SCBD2	Excited State 1: Singlet-A	2.0992 eV	590.64 nm	f=0.0001	<S**2>=0.000
	94 -> 95	0.70321			
	94 <- 95	-0.10830			
SCBD3	Excited State 1: Singlet-A	2.4152 eV	513.35 nm	f=0.0001	<S**2>=0.000
	92 -> 93	0.70681			
SCBD4	Excited State 1: Singlet-A	2.6179 eV	473.59 nm	f=0.0000	<S**2>=0.000
	84 -> 85	0.70474			

Table S13. The $\Delta E(S_1-T_1)_{va}$ of CBD and substituted CBDs (SCBD).

	$\Delta E(S_1-T_1)_{va}$
CBD	2.19
SCBD1	2.19
SCBD2	1.78
SCBD3	1.89
SCBD4	1.88

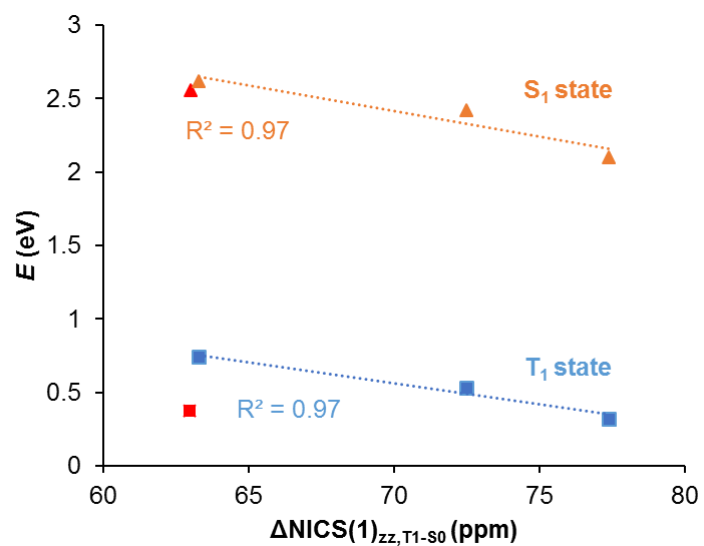


Figure S7. Dependence of $E(T_1)$ and $E(S_1)$ on $\Delta\text{NICS}(1)_{\text{zz}, \text{T1-S0}}$ of the **SCBD** derivatives. R^2 is the squared correlation coefficient. The correlation does not include the red points which correspond to **SCBD1**. Calculations at M06-2X/6-311+G(d,p).

SUBSTITUTED PENTALENES

Weights of the singly excited HOMO to LUMO configurations of substituted pentalenes
In all cases the major configuration in the S_1 state is the HOMO to LUMO transition.

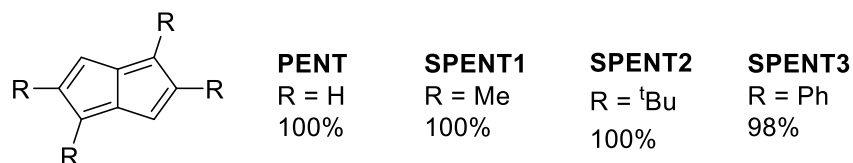


Figure S8. Percentage of the singly excited HOMO to LUMO configuration in the S_1 state of pentalene (**PENT**) and substituted pentalenes (**SPENT**).

Table S14. Coefficients of the major configurations from the Gaussian output of pentalene and the substituted pentalenes (**SPENT1** - **SPENT4**).

PENT	Excited State 1: Singlet-A 27 -> 28	0.71079	1.8917 eV	655.43 nm	f=0.0000	<S**2>=0.000
SPENT1	Excited State 1: Singlet-A 43 -> 44	0.70925	1.9308 eV	642.14 nm	f=0.0000	<S**2>=0.000
SPENT2	Excited State 1: Singlet-A 91 -> 92	0.70861	1.8166 eV	682.52 nm	f=0.0001	<S**2>=0.000
SPENT3	Excited State 1: Singlet-A 99 -> 108 107 -> 108	-0.11086 0.69600	1.5529 eV	798.42 nm	f=0.0001	<S**2>=0.000

Table S15. $\Delta E(S_1-T_1)_{va}$ of pentalene (**PENT**) and substituted pentalenes (**SPENT**).

	$\Delta E(S_1-T_1)_{va}$
PENT	1.26
SPENT1	1.33
SPENT2	1.22
SPENT3	1.07

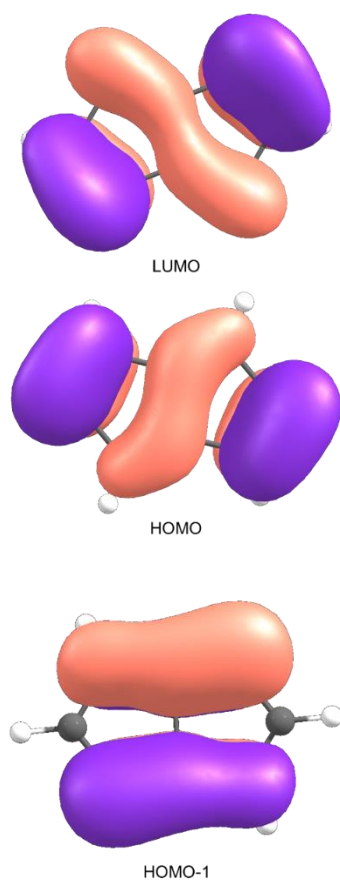


Figure S9. HOMO-1, HOMO and LUMO of the parent pentalene calculated at M06-2X/6-311+G(d,p) level.

SUBSTITUTED INDACENES

Weights of the singly excited HOMO to LUMO configurations of substituted *as*- and *s*-indacenes. In all the cases the major configuration in the S_1 state is the HOMO to LUMO transition.

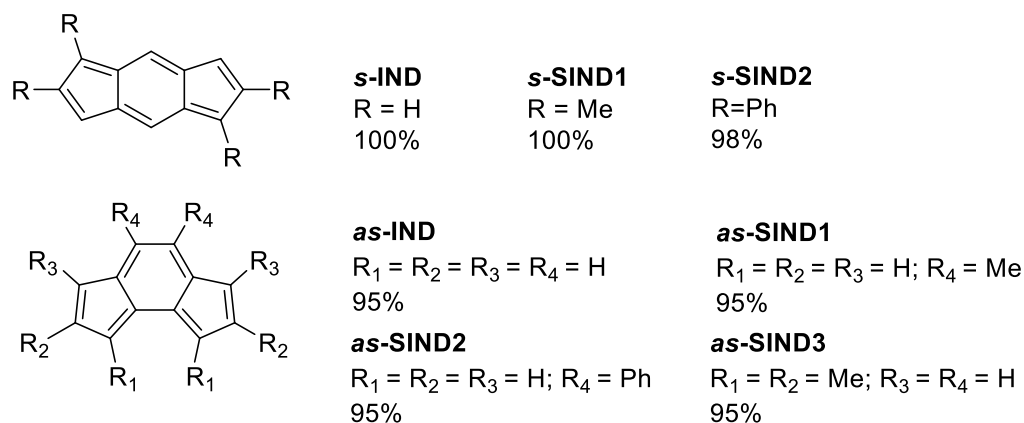


Figure S10. Percentage of the singly excited HOMO to LUMO configuration in the S_1 state of *s*- and *as*-indacenes and substituted derivatives.

Table S16. Coefficients of the major configurations from Gaussian output of *s*- and *as*-indacenes and substituted derivatives.

s-IND	Excited State 1: Singlet-AG <S**2>=0.000 40 -> 41 0.70765	1.6716 eV 741.70 nm f=0.0000
s-SIND1	Excited State 1: Singlet-A <S**2>=0.000 56 -> 57 0.70683	1.8081 eV 685.72 nm f=0.0000
s-SIND2	Excited State 1: Singlet-A <S**2>=0.000 120 -> 121 0.69690	1.5378 eV 806.25 nm f=0.0000
as-IND	Excited State 1: Singlet-B2 <S**2>=0.000 39 -> 41 0.16152 40 -> 41 0.69091	1.5509 eV 799.41 nm f=0.0092
as-SIND1	Excited State 1: Singlet-A <S**2>=0.000 47 -> 49 0.16615 48 -> 49 0.68925	1.6079 eV 771.12 nm f=0.0103
as-SIND2	Excited State 1: Singlet-A <S**2>=0.000 79 -> 81 0.15058 80 -> 81 0.69153	1.5184 eV 816.52 nm f=0.0109
as-SIND3	Excited State 1: Singlet-B <S**2>=0.000 55 -> 57 -0.17151 56 -> 57 0.68633	1.7056 eV 726.94 nm f=0.0071

With regard to *s*-indacenes, they satisfy the $2E(T_1) < E(S_1)$ criterion, but $E(T_2)$ is so far below $E(S_1)$ that none of the substituted *s*-indacenes are suitable. In contrast, both singlet fission criteria are satisfied in the parent and in several substituted *as*-indacenes, yet these compounds have very low $E(T_1)$. Combined, this suggests that indacenes are not suitable for singlet fission, at least not in connection to silicon solar cell technology.

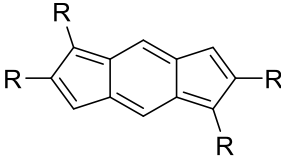
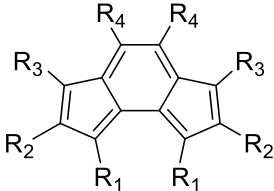
	R = H (<i>s</i>-IND)	R = Me (<i>s</i>-SIND1)	R = Ph (<i>s</i>-SIND2)
	$E(T_1)_a = 0.72$	$E(T_1)_a = 0.75$	$E(T_1)_a = 0.67$
	$E(S_1)_v = 1.67$	$E(S_1)_v = 1.81$	$E(S_1)_v = 1.54$
	$E(T_2)_v = 1.21$	$E(T_2)_v = 1.28$	$E(T_2)_v = 1.14$
	$E(S_1)_v/E(T_1)_a = 2.32$	$E(S_1)_v/E(T_1)_a = 2.41$	$E(S_1)_v/E(T_1)_a = 2.30$
	R₁ = R₂ = R₃ = R₄ = H (<i>as</i>-IND)	R₁ = R₂ = R₃ = H; R₄ = Me (<i>as</i>-SIND1)	
	$E(T_1)_a = 0.14$	$E(T_1)_a = 0.22$	
	$E(S_1)_v = 1.55$	$E(S_1)_v = 1.61$	
	$E(T_2)_v = 1.94$	$E(T_2)_v = 1.57$	
	$E(S_1)_v/E(T_1)_a = 11.07$	$E(S_1)_v/E(T_1)_a = 7.32$	
	R₁ = R₂ = R₃ = H; R₄ = Ph (<i>as</i>-SIND2)	R₁ = R₂ = Me; R₃ = R₄ = H (<i>as</i>-SIND3)	
	$E(T_1)_a = 0.14$	$E(T_1)_a = 0.30$	
	$E(S_1)_v = 1.52$	$E(S_1)_v = 1.71$	
	$E(T_2)_v = 1.54$	$E(T_2)_v = 1.44$	
	$E(S_1)_v/E(T_1)_a = 10.86$	$E(S_1)_v/E(T_1)_a = 5.70$	

Figure S11. The parent and substituted *s*- and *as*-indacenes and their excitation energies (in eV) computed at TD-M06-2X/def2-TZVPD//M06-2X/6-311+G(d,p) level.

Table S17. The $\Delta E(S_1-T_1)_{va}$ of *s*- and *as*-indacenes and substituted derivatives.

	$\Delta E(S_1-T_1)_{va}$
<i>s</i>-IND	0.95
<i>s</i>-SIND1	1.06
<i>s</i>-SIND2	0.87
<i>as</i>-IND	1.41
<i>as</i>-SIND1	1.39
<i>as</i>-SIND2	1.38
<i>as</i>-SIND3	1.41

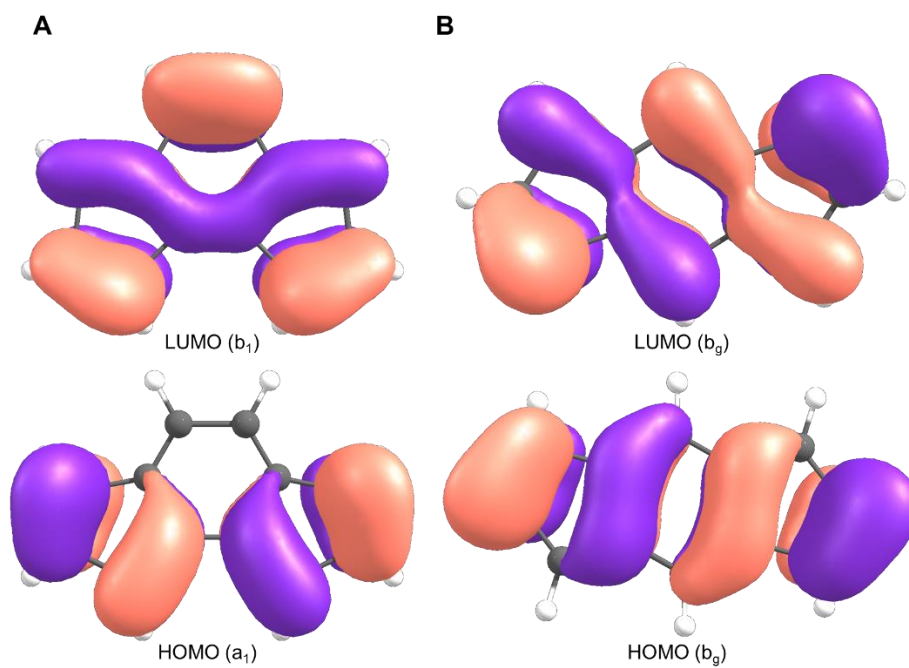


Figure S12. HOMO and LUMO of the parent *s*-indacene (A) and *as*-indacene (B) obtained at M06-2X/6-311+G(d,p). Symmetries are given in parenthesis.

BENZANNELATED CBDs

Weights of the major configurations of substituted **BENZCBDs**. In all cases except **BENZCBD7** the major configuration in the S_1 state is the HOMO to LUMO transition.

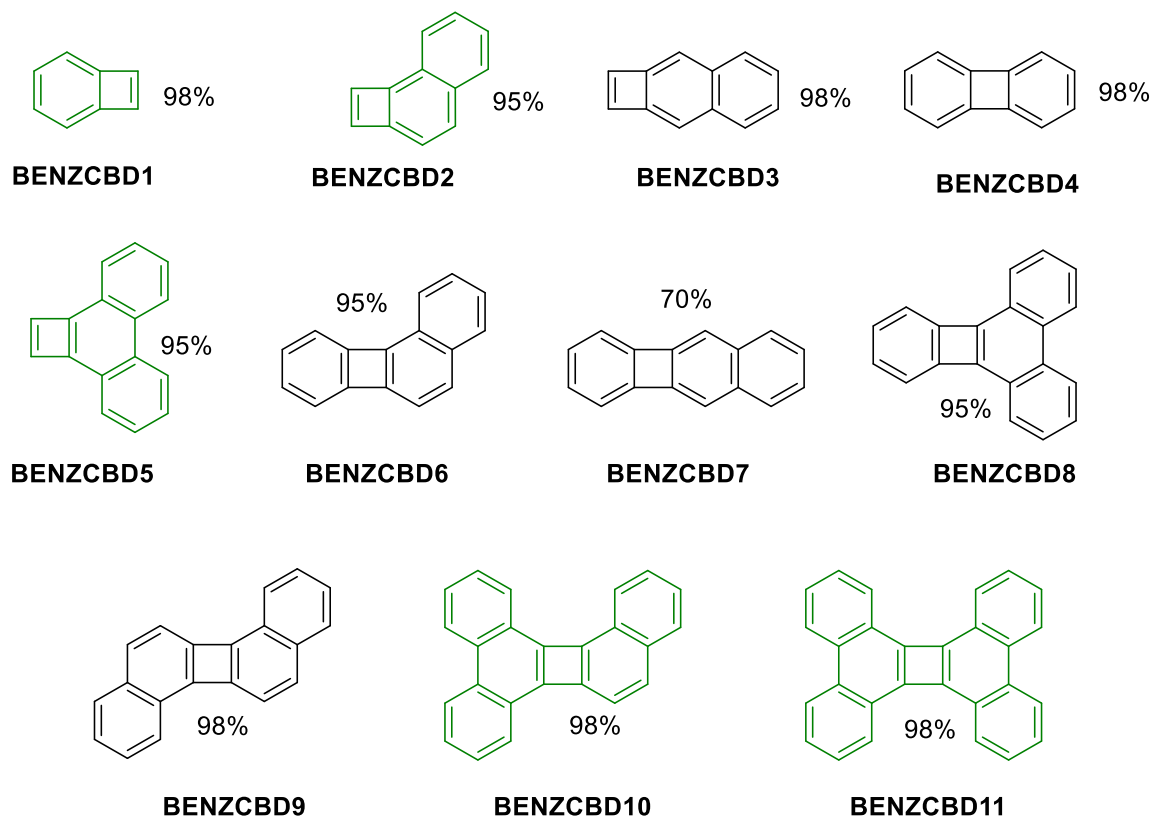


Figure S13. Percentage of the singly excited HOMO to LUMO configuration in the S_1 state of benzannelated CBDs (BENZCBD).

Table S18. Coefficients of the major configurations from Gaussian output of benzannelated CBDs (BENZCBD) derivatives.

BENZCBD1	Excited State 1:	Singlet-B2	3.1464 eV	394.05 nm	f=0.0003
	<S**2>=0.000				
	27 -> 28	0.70546			
BENZCBD2	Excited State 1:	Singlet-A'	2.5678 eV	482.84 nm	f=0.0056
	<S**2>=0.000				
	40 -> 41	0.68931			
BENZCBD3	Excited State 1:	Singlet-B2	3.4082 eV	363.78 nm	f=0.0021
	<S**2>=0.000				
	40 -> 41	0.69960			
BENZCBD4	Excited State 1:	Singlet-B2	3.5941 eV	344.96 nm	f=0.0000
	<S**2>=0.000				
	40 -> 41	0.70153			
BENZCBD5	Excited State 1:	Singlet-B2	2.3528 eV	526.96 nm	f=0.0293
	<S**2>=0.000				
	50 -> 54	-0.10722			

	53 -> 54	0.68787				
	53 -> 58	0.12273				
BENZCBD6	Excited State <S**2>=0.000	1: Singlet-A'	3.0363 eV	408.35 nm	f=0.0121	
	53 -> 54	0.68582				
BENZCBD7	Excited State <S**2>=0.000	1: Singlet-A1	3.9019 eV	317.76 nm	f=0.1300	
	52 -> 55	-0.35803				
	53 -> 54	0.58997				
BENZCBD8	Excited State <S**2>=0.000	1: Singlet-B2	2.8436 eV	436.01 nm	f=0.0416	
	66 -> 67	0.68748				
	66 -> 73	0.11588				
BENZCBD9	Excited State <S**2>=0.000	1: Singlet-AG	2.5661 eV	483.16 nm	f=0.0000	
	66 -> 67	0.69558				
BENZCBD10	Excited State <S**2>=0.000	1: Singlet-A'	2.3637 eV	524.54 nm	f=0.0106	
	79 -> 80	0.69583				
BENZCBD11	Excited State <S**2>=0.000	1: Singlet-B3G	2.1581 eV	574.50 nm	f=0.0000	
	92 -> 93	0.69816				

Table S19. Oscillator strengths for the S₁ transition of benzannelated CBDs (**BENZCBD**).

	f
BENZCBD1	0.003
BENZCBD2	0.006
BENZCBD3	0.002
BENZCBD4	0.000
BENZCBD5	0.029
BENZCBD6	0.012
BENZCBD7	0.130
BENZCBD8	0.042
BENZCBD9	0.000
BENZCBD10	0.011
BENZCBD11	0.000

Table S20. The $\Delta E(S_1-T_1)_{va}$, $\Delta E(S_1-T_1)_{vv}$, $E(S_1)/E(T_1)_a$ and $E(S_1)/E(T_1)_v$ of benzannelated CBDs (**BENZCBD**). The subscripts a, v, va and vv stand for adiabatic, vertical, vertical-adiabatic and vertical-vertical. The average $\Delta E(S_1-T_1)_{va}$ is 1.36 eV.

	$\Delta E(S_1-T_1)_{va}$	$\Delta E(S_1-T_1)_{vv}$	$E(S_1)/E(T_1)_a$	$E(S_1)/E(T_1)_v$
BENZCBD1	1.69	0.79	2.17	1.33
BENZCBD2	1.59	0.79	2.62	1.33
BENZCBD3	1.57	1.01	1.85	1.42
BENZCBD4	1.31	0.90	1.57	1.33
BENZCBD5	1.61	0.82	3.18	1.33
BENZCBD6	1.27	0.92	1.73	1.44
BENZCBD7	0.94	0.99	1.32	1.34
BENZCBD8	1.29	0.92	1.83	1.48
BENZCBD9	1.22	0.89	1.90	1.53
BENZCBD10	1.22	0.65	2.08	1.38
BENZCBD11	1.25	0.66	2.36	1.44

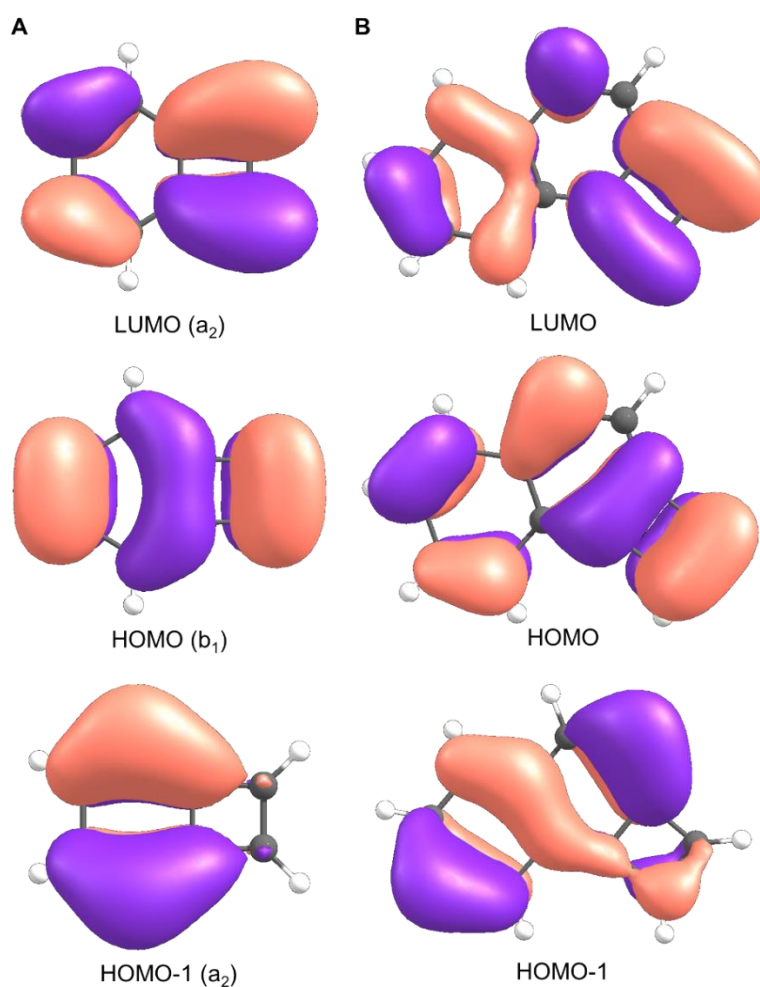


Figure S14. HOMO-1, HOMO and LUMO of **BENZCBD1** (A) and **BENZCBD2** (B) obtained at M06-2X/6-311+G(d,p). Orbital symmetries are in parenthesis.

Energy tuning of BENZCBD2 by structural distortion

Despite being suitable as singlet fission chromophore the bent naphthoCBD has a calculated $E(T_1)$ which is ~ 0.2 eV below the ideal $E(T_1)$ value. To examine if $E(T_1)$ can be increased this tunability we regarded the C₈-C₉ bond and investigated if an elongation of this bond stabilizes HOMO due to lessened antibonding character and destabilize LUMO due to lessened bonding character. Yet, in contrast to the observation made for fulvenes, bond length distortions did not extensively impact on $E(T_1)$, $E(S_1)$ and $E(T_2)$ of naphthoCBD (Figure S15). The maximal change in $E(T_1)$ and $E(S_1)$ are 0.18 and 0.14 eV, respectively. Thus, bond length distortions as a design tool is inefficient for PAAHs (also small PAAHs) as the frontier orbitals extend over too many bonds leading to only small relative impact from each bond on the orbital energy.

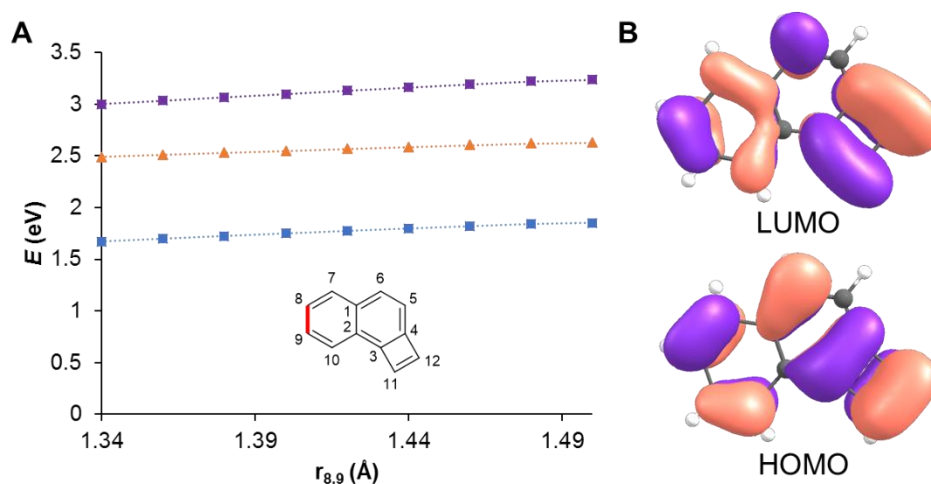


Figure S15. (A) The $E(T_1)_v$, $E(S_1)$ and $E(T_2)$ energies of bent **BENZCBD2** as a function of the $r_{C_8-C_9}$ distance, and (B) HOMO and LUMO for the S_0 state. Computations at TD-M06-2X/def2-TZVPD//((U)M06-2X/6-311+G(d,p) level.

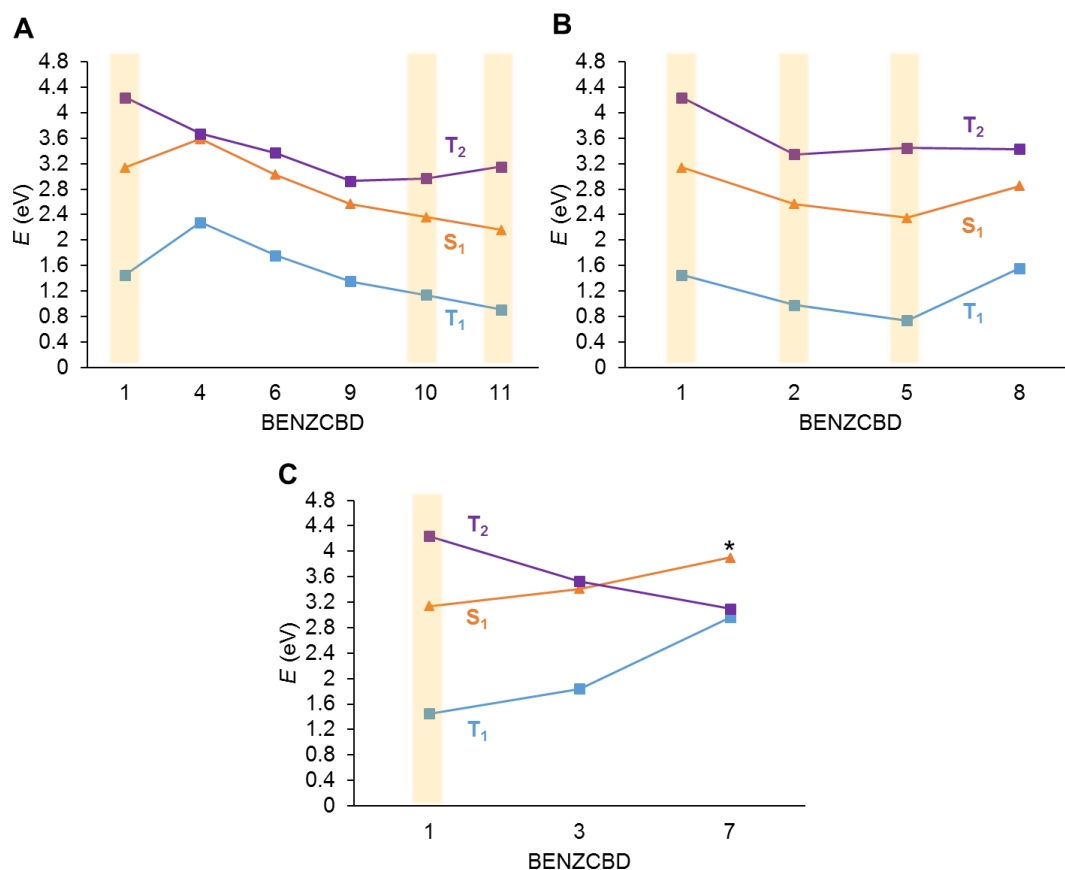


Figure S16. The variation in $E(T_1)_a$, $E(S_1)$ and $E(T_2)$ as a function of benzannulation in selected benzannulated CBDs. Computations at TD-M06-2X/def2-TZVPD//((U)M06-2X/6-311+G(d,p) level. The * at the $E(S_1)$ value of **BENZCBD7** indicates the two-configurational character of this state, leading to an energy lowering.

Table S21: HOMA values of CBD and of the CBD unit in benzannulated CBDs in the T1 state.

	HOMA
CBD	0.41
BENZCBD1	0.02
BENZCBD2	0.28
BENZCBD3	-0.33
BENZCBD4	-0.16
BENZCBD5	0.41
BENZCBD6	-0.09
BENZCBD7	0.14
BENZCBD8	0.03
BENZCBD9	0.13
BENZCBD10	0.21
BENZCBD11	0.27

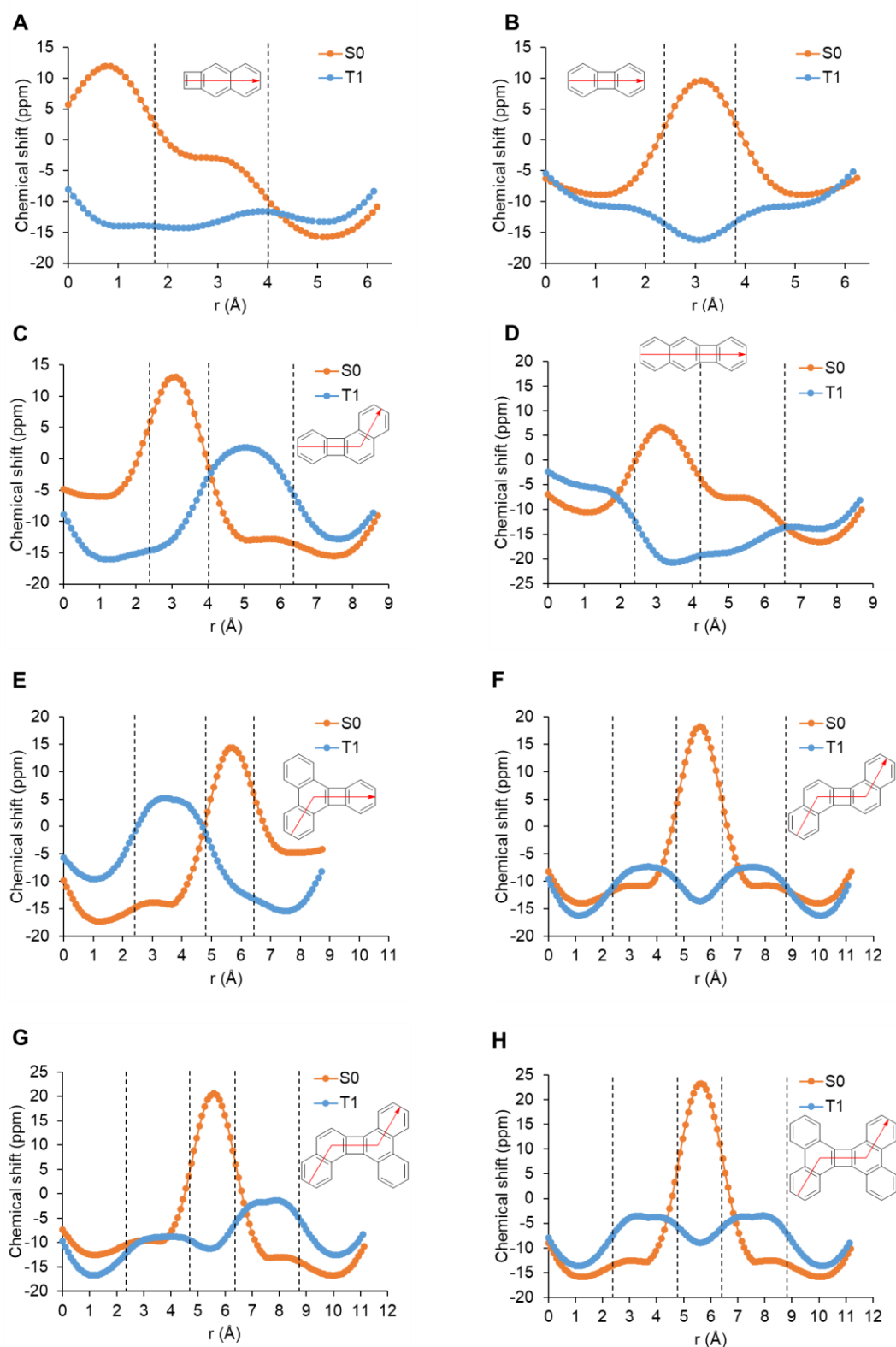


Figure S17. NICS-XY scans of (A) **BENZCBD3**, (B) **BENZCBD4**, (C) **BENZCBD6**, (D) **BENZCBD7**, (E) **BENZCBD8**, (F) **BENZCBD9**, (G) **BENZCBD10** and (H) **BENZCBD11** in their S_0 and T_1 states calculated at GIAO/M06-2X/6-311+G(d,p) level.

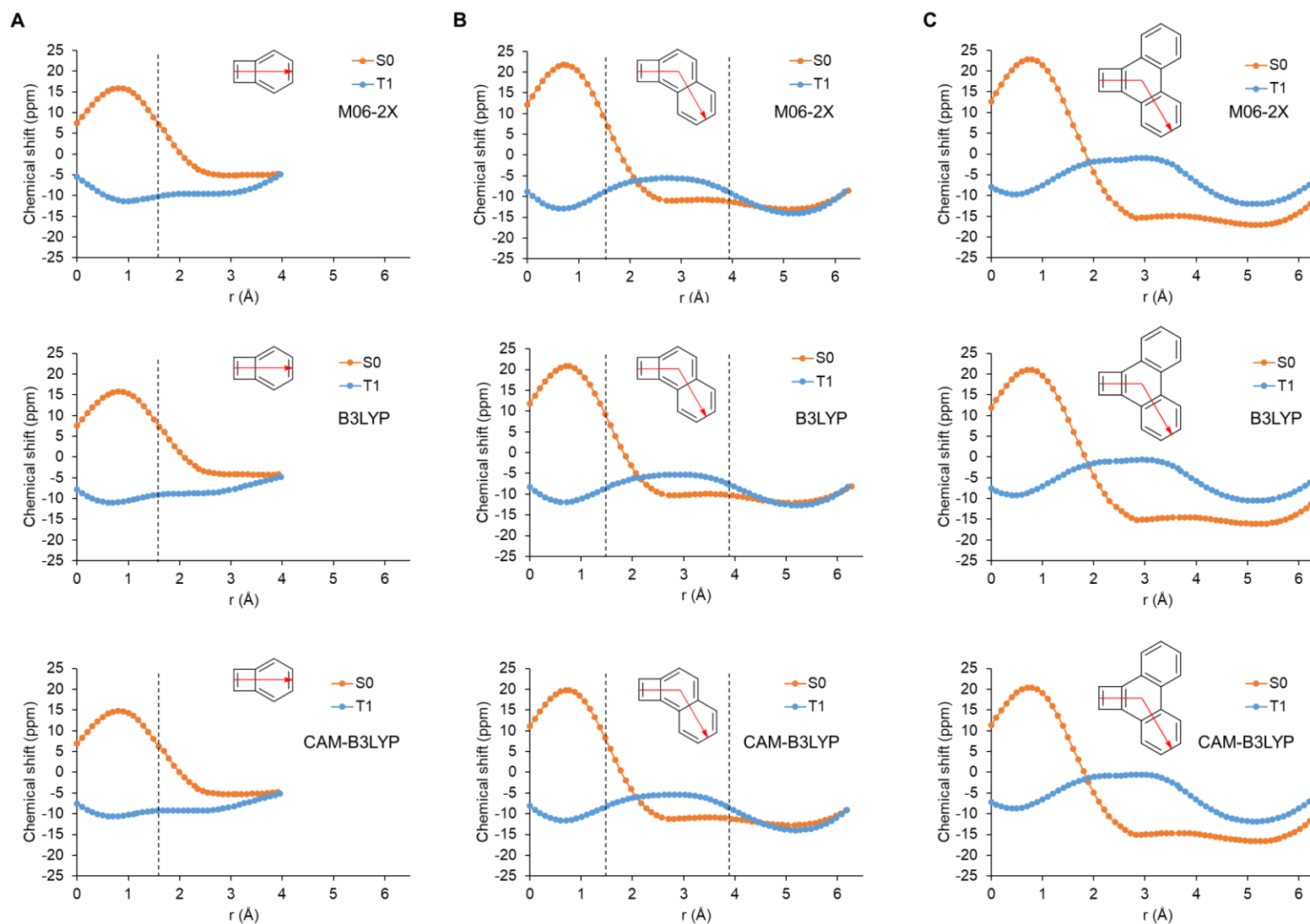


Figure S18. Comparison of NICS-XY scans of (A) **BENZCBD1**, (B) **BENZCBD2** and (C) **BENZCBD5** using M06-2X, B3LYP and CAM-B3LYP.

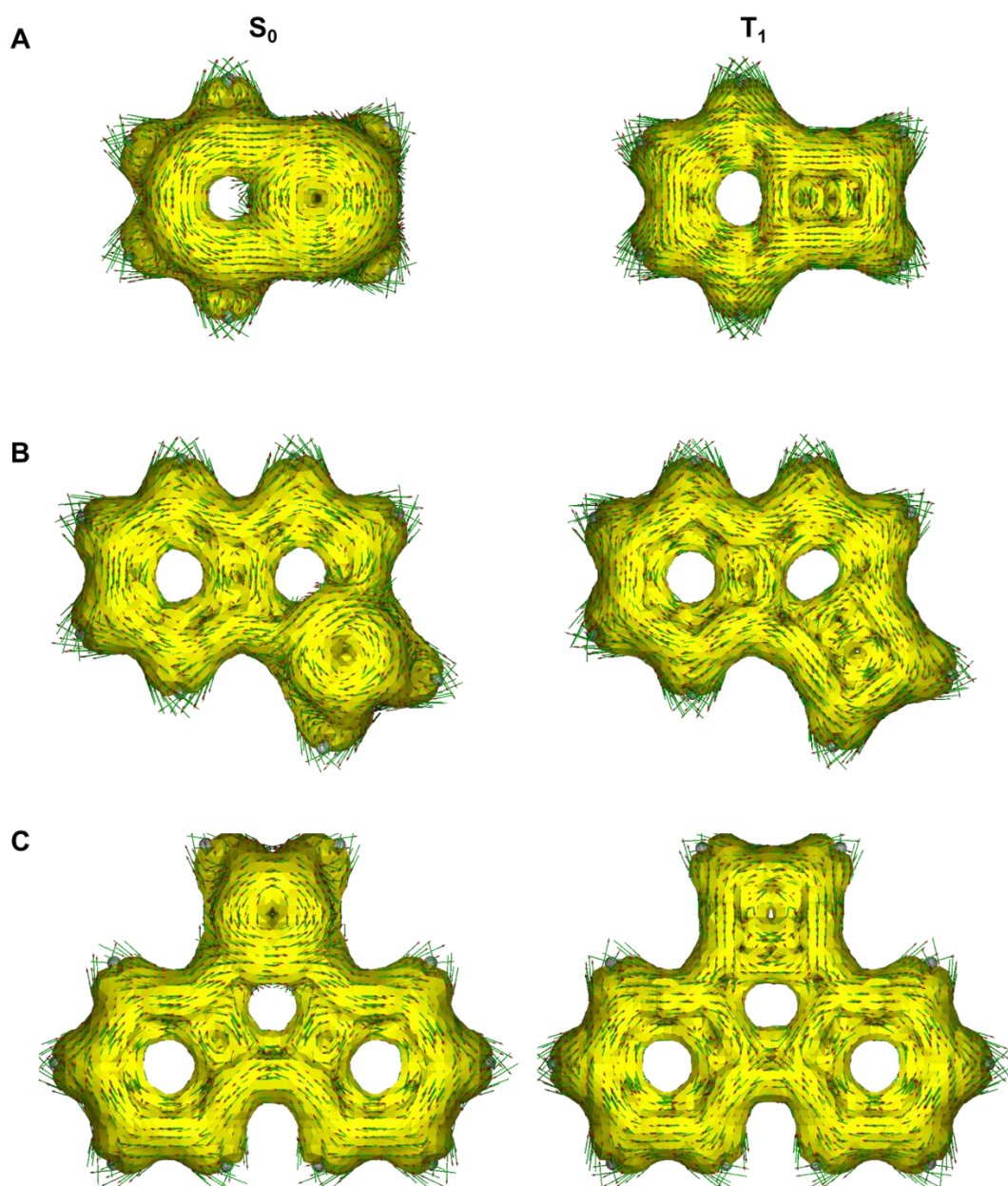
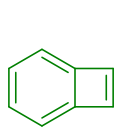


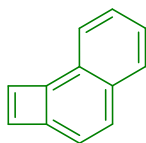
Figure S19. ACID of **BENZOCBD1**, **BENZOCBD2** and **BENZCBD5** in their S_0 and T_1 states calculated at TD-M06-2X/def2-TZVPD//M06-2X/6-311+G(d,p) level.

Full IUPAC names of the benzannelated CBDs



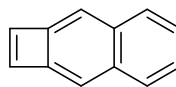
BENZCBD1

benzocyclobutadiene



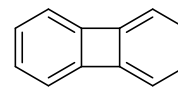
BENZCBD2

cyclobuta[a]naphthalene



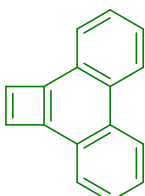
BENZCBD3

cyclobuta[b]naphthalene



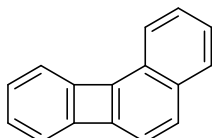
BENZCBD4

biphenylene



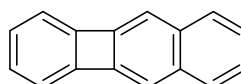
BENZCBD5

cyclobuta[l]phenanthrene



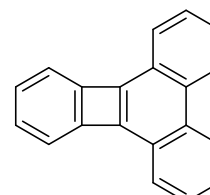
BENZCBD6

benzo[a]biphenylene



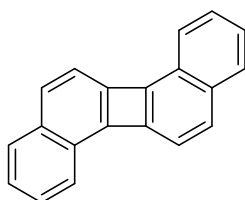
BENZCBD7

benzo[b]biphenylene



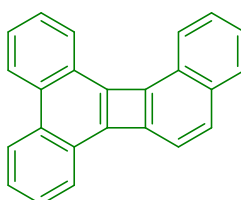
BENZCBD8

benzo[3,4]cyclobuta-
-[1,2-l]phenanthrene



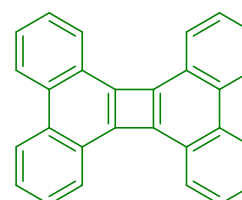
BENZCBD9

dibenzo[a,g]biphenylene



BENZCBD10

naphtho[1',2':3,4]cyclobuta-
-[1,2-l]phenanthrene



BENZCBD11

cyclobuta[1,2-l:3,4-l']-
-diphenanthrene

Figure S20. Full IUPAC names of the BENZCBDs.

BENZANNELATED PENTALENES

Weights of the singly excited HOMO to LUMO configurations of substituted BENZPENTs. In all cases except one the major configuration in the S_1 state is the HOMO to LUMO transition. The exception is **BENZPENT10** for which the S_1 transition is a two-configurational transition described by the HOMO-2 to LUMO configuration (63%) and HOMO to LUMO (37%).

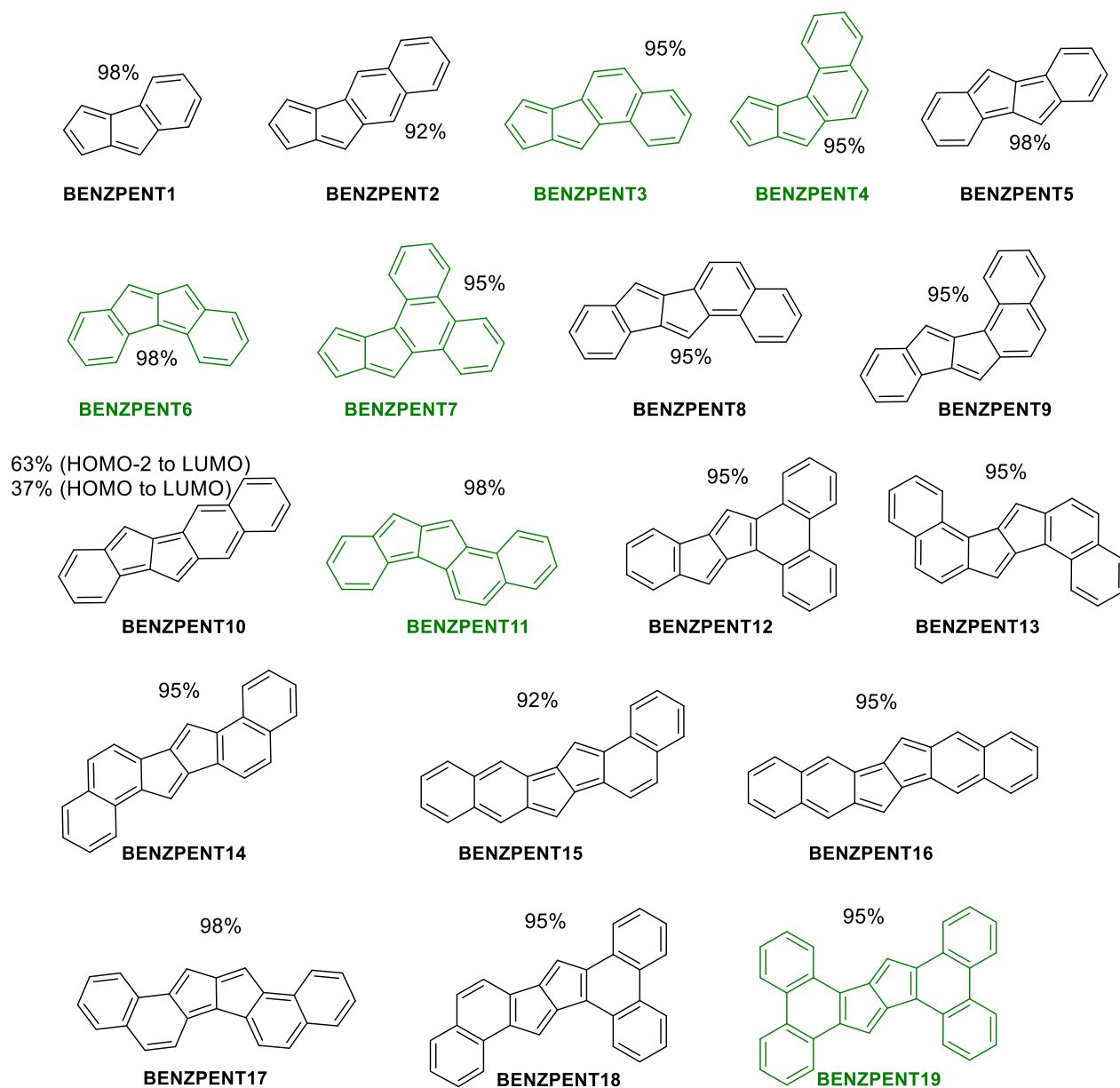


Figure S21. Percentage the singly excited HOMO to LUMO configuration in the S_1 state of benzannelated pentalenes (BENZPENT).

Table S22. Coefficients of the major configurations from Gaussian output of benzannelated pentalenes (BENZPENT).

BENZPENT1	Excited State 1: Singlet-A' 2.2967 eV 539.84 nm f=0.0007 <S**2>=0.000 40 -> 41 0.70549
BENZPENT2	Excited State 1: Singlet-A' 2.4837 eV 499.19 nm f=0.0065 <S**2>=0.000 52 -> 54 0.18111 53 -> 54 0.67621
BENZPENT3	Excited State 1: Singlet-A' 1.9743 eV 628.00 nm f=0.0006 <S**2>=0.000 51 -> 54 -0.10499 52 -> 54 0.10685 53 -> 54 0.68813
BENZPENT4	Excited State 1: Singlet-A' 1.9548 eV 634.26 nm f=0.0010 <S**2>=0.000 51 -> 54 0.13553 53 -> 54 0.69017
BENZPENT5	Excited State 1: Singlet-AG 2.6866 eV 461.50 nm f=0.0000 <S**2>=0.000 53 -> 54 0.70286
BENZPENT6	Excited State 1: Singlet-A' 1.2760 eV 971.66 nm f=0.0060 <S**2>=0.000 53 -> 54 0.70478
BENZPENT7	Excited State 1: Singlet-A' 1.8178 eV 682.07 nm f=0.0051 <S**2>=0.000 63 -> 67 -0.10523 66 -> 67 0.68837
BENZPENT8	Excited State 1: Singlet-A' 2.3423 eV 529.33 nm f=0.0042 <S**2>=0.000 66 -> 67 0.68727
BENZPENT9	Excited State 1: Singlet-A' 2.3177 eV 534.94 nm f=0.0020 <S**2>=0.000 64 -> 67 -0.10364 66 -> 67 0.69199
BENZPENT10	Excited State 1: Singlet-A' 2.8843 eV 429.86 nm f=0.0091 <S**2>=0.000 65 -> 67 0.56288 66 -> 67 -0.41235
BENZPENT11	Excited State 1: Singlet-A' 1.5869 eV 781.30 nm f=0.0036 <S**2>=0.000 66 -> 67 0.69908
BENZPENT12	Excited State 1: Singlet-A' 2.1771 eV 569.49 nm f=0.0111 <S**2>=0.000 79 -> 80 0.69072
BENZPENT13	Excited State 1: Singlet-A' 2.0172 eV 614.62 nm f=0.0000 <S**2>=0.000 79 -> 80 0.69368

BENZPENT14	Excited State 1: Singlet-A' 2.0538 eV 603.68 nm f=0.0000 <S**2>=0.000 79 -> 80 0.69332
BENZPENT15	Excited State 1: Singlet-A' 2.5063 eV 494.68 nm f=0.0200 <S**2>=0.000 78 -> 80 0.15391 79 -> 80 0.67583
BENZPENT16	Excited State 1: Singlet-AG 3.1111 eV 398.52 nm f=0.0000 <S**2>=0.000 78 -> 80 0.69215
BENZPENT17	Excited State 1: Singlet-A 1.3222 eV 937.72 nm f=0.0007 <S**2>=0.000 79 -> 80 0.70128
BENZPENT18	Excited State 1: Singlet-A' 1.9090 eV 649.46 nm f=0.0027 <S**2>=0.000 92 -> 93 0.69350
BENZPENT19	Excited State 1: Singlet-AG 1.7736 eV 699.04 nm f=0.0000 <S**2>=0.000 105 -> 106 0.69423

Table S23. Oscillator strengths for the S₁ transition of benzannelated pentalenes (BENZPENT).

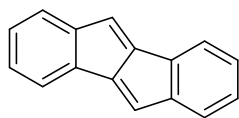
	f
BENZPENT1	0.007
BENZPENT2	0.007
BENZPENT3	0.001
BENZPENT4	0.010
BENZPENT5	0.000
BENZPENT6	0.006
BENZPENT7	0.005
BENZPENT8	0.004
BENZPENT9	0.002
BENZPENT10	0.009
BENZPENT11	0.036
BENZPENT12	0.011
BENZPENT13	0.020
BENZPENT14	0.000
BENZPENT15	0.020
BENZPENT16	0.000
BENZPENT17	0.001
BENZPENT18	0.003
BENZPENT19	0.000

Table S24. The $\Delta E(S_1-T_1)_{va}$, $\Delta E(S_1-T_1)_{vv}$, $E(S_1)/E(T_1)_a$ and $E(S_1)/E(T_1)_v$ of pentalene (PENT) and benzannelated pentalenes (BENZPENT). The subscripts a, v, va and vv stand for adiabatic, vertical, vertical-adiabatic and vertical-vertical. The average $\Delta E(S_1-T_1)_{va}$ is 1.08 eV.

	$\Delta E(S_1-T_1)_{va}$	$\Delta E(S_1-T_1)_{vv}$	$E(S_1)/E(T_1)_a$	$E(S_1)/E(T_1)_v$
PENT	1.26	0.80	3.00	1.73
BENZPENT1	1.26	0.73	2.21	1.46
BENZPENT2	1.34	0.75	2.16	1.43
BENZPENT3	1.11	0.44	2.30	1.29
BENZPENT4	0.93	0.44	2.11	1.29
BENZPENT5	0.99	0.62	1.58	1.30
BENZPENT6	1.16	0.57	10.74	1.80
BENZPENT7	1.08	0.44	2.49	1.32
BENZPENT8	1.01	0.63	1.76	1.37
BENZPENT9	0.99	0.63	1.74	1.37
BENZPENT10	1.12	0.71	1.63	1.33
BENZPENT11	1.08	0.50	3.11	1.46
BENZPENT12	1.02	0.57	1.88	1.35
BENZPENT13	0.93	0.61	1.85	1.43
BENZPENT14	0.93	0.6	1.83	1.41
BENZPENT15	1.09	0.66	1.76	1.36
BENZPENT16	1.31	0.99	1.73	1.47
BENZPENT17	0.93	0.58	3.39	1.78
BENZPENT18	0.94	0.61	1.96	1.47
BENZPENT19	1.11	0.39	2.32	1.28

Table S25: HOMA values of pentalene (PENT) and of the pentalene unit in benzannelated pentalenes (BENZPENT) in the T_1 state.

	HOMA
PENT	0.86
BENZPENT1	0.37
BENZPENT2	0.37
BENZPENT3	0.72
BENZPENT4	0.73
BENZPENT5	0.51
BENZPENT6	0.42
BENZPENT7	0.80
BENZPENT8	0.47
BENZPENT9	0.54
BENZPENT10	0.23
BENZPENT11	0.49
BENZPENT12	0.54
BENZPENT13	0.68
BENZPENT14	0.67
BENZPENT15	0.30
BENZPENT16	0.42
BENZPENT17	0.60
BENZPENT18	0.70
BENZPENT19	0.75



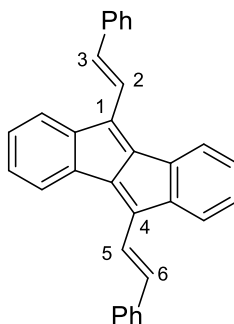
BENZPENT5

$$E(T_1)_a = 1.70$$

$$E(S_1)_v = 2.69$$

$$E(T_2)_v = 2.18$$

$$E(S_1)_v/E(T_1)_a = 1.58$$



bis(styryl)BENZPENT5

$$E(T_1)_a = 1.21$$

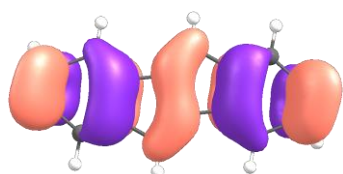
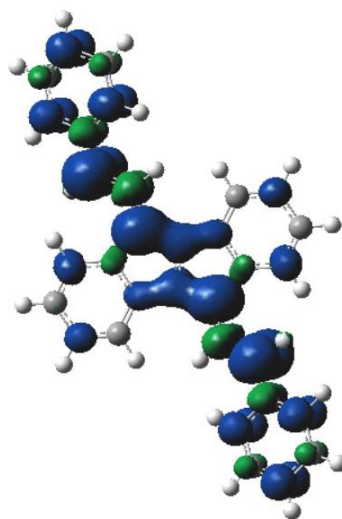
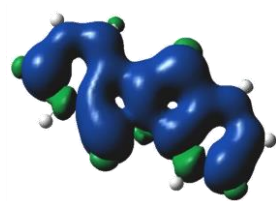
$$E(S_1)_v = 2.46$$

$$E(T_2)_v = 2.02$$

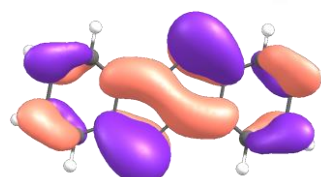
$$E(S_2)_v = 2.81$$

$$E(S_1)_v/E(T_1)_a = 2.04$$

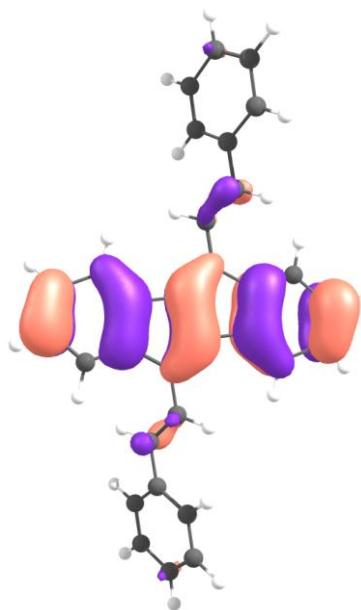
$$E(S_2)_v/E(T_1)_a = 2.32$$



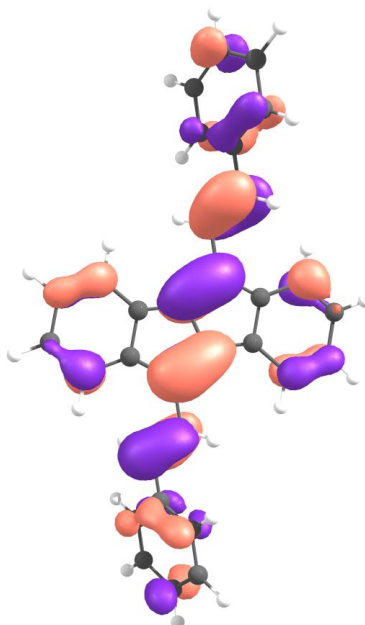
HOMO



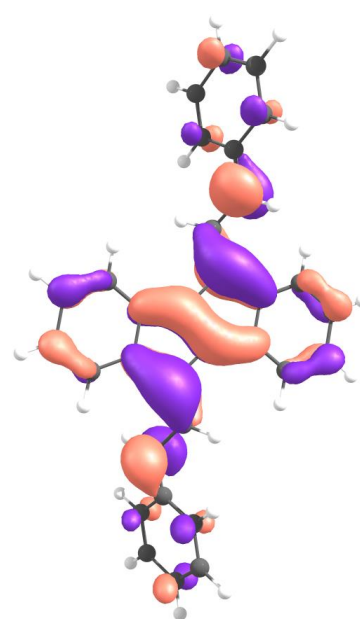
LUMO



HOMO-1



HOMO



LUMO

Figure S22. Electronic excitation energies (eV) and spin density of **BENZPENT5**, **bis(styryl)BENZPENT5** and **BENZPENT20**. Computations at TD-M06-2X/def2-TZVPD//((U)M06-2X/6-311+G(d,p) level.

Bis(styryl)BENZPENT5 has shown to provide an entry point to singlet fission as the excitation occurs in the S_2 state, and such molecule compared to **BENZPENT5** satisfies the criteria. The spin density is accumulated on the pentalene unit in the case of **BENZPENT5** while in **bis(styryl)BENZPENT5**, it is concentrated on C1/C4 and C3/C6. For **BENZPENT5**, the S_1 excitation is from HOMO to LUMO, yet for **bis(styryl)BENZPENT5**, the excitation is from HOMO-1 to LUMO. Yet, as the S_1 state of **bis(styryl)BENZPENT5** has double excitation character, TD-DFT is not suitable to describe the excitation energies. As a comparison, for 1,8-diphenyloctatetraene, $E(S_1) = 3.37$ eV and $E(T_1) = 1.88$ eV; for **bis(styryl)BENZPENT5**, $E(S_1) = 2.46$ eV and $E(T_1) = 1.59$ eV; for **BENZPENT5**, $E(S_1) = 2.69$ eV and $E(T_1) = 2.07$ eV.

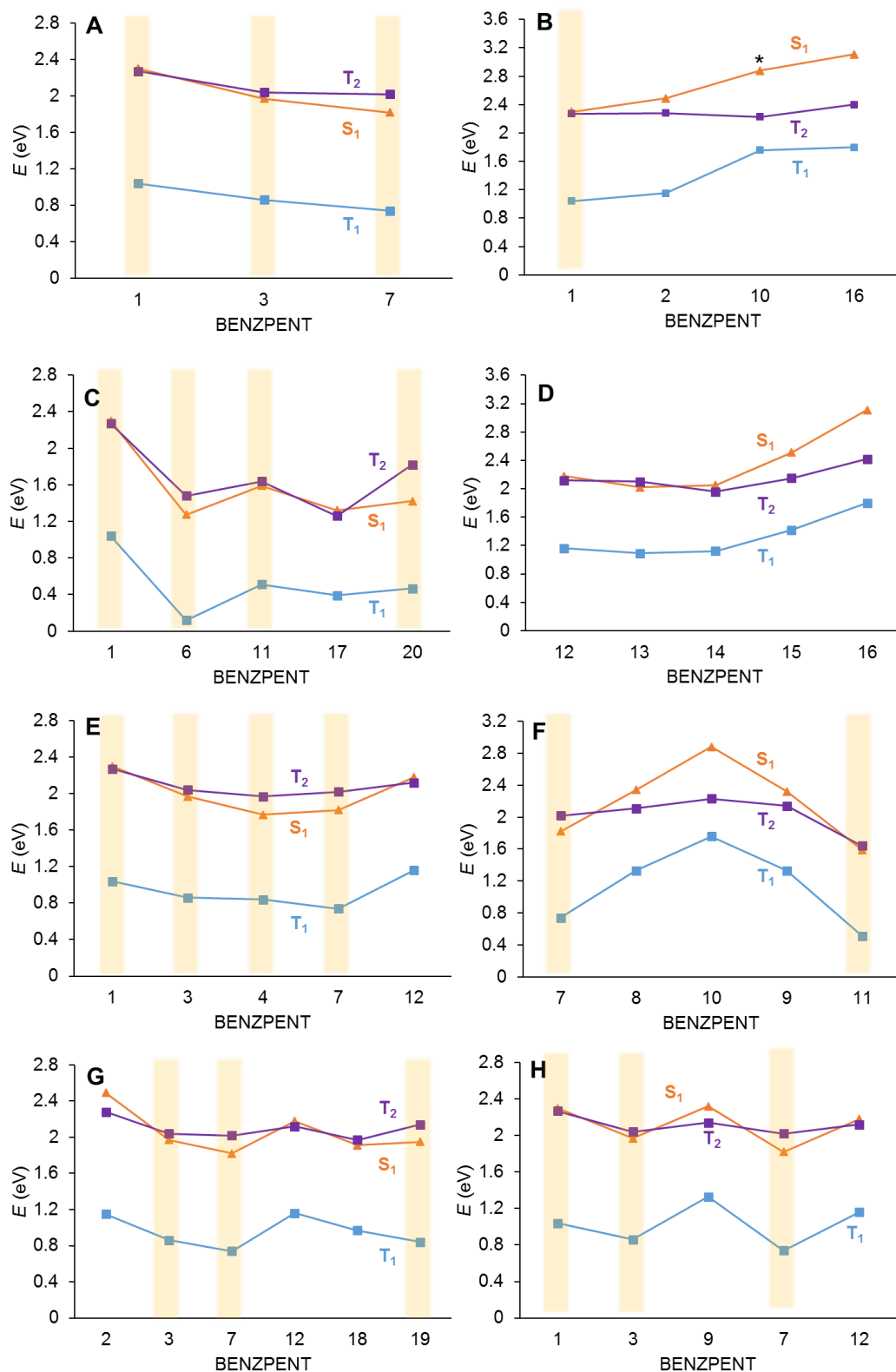


Figure S23. Additional plots of the variations in $E(T_1)_a$, $E(S_1)$ and $E(T_2)$ as functions of benzannellation in selected benzannelated pentalenes. Computations at TD-M06-2X/def2-TZVPD//((U)M06-2X/6-311+G(d,p) level.

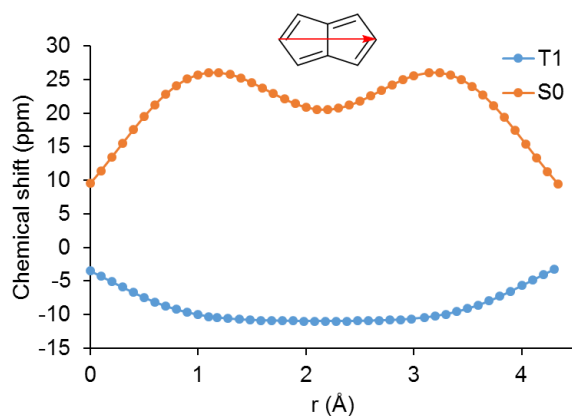


Figure S24. NICS-XY scan of pentalene.

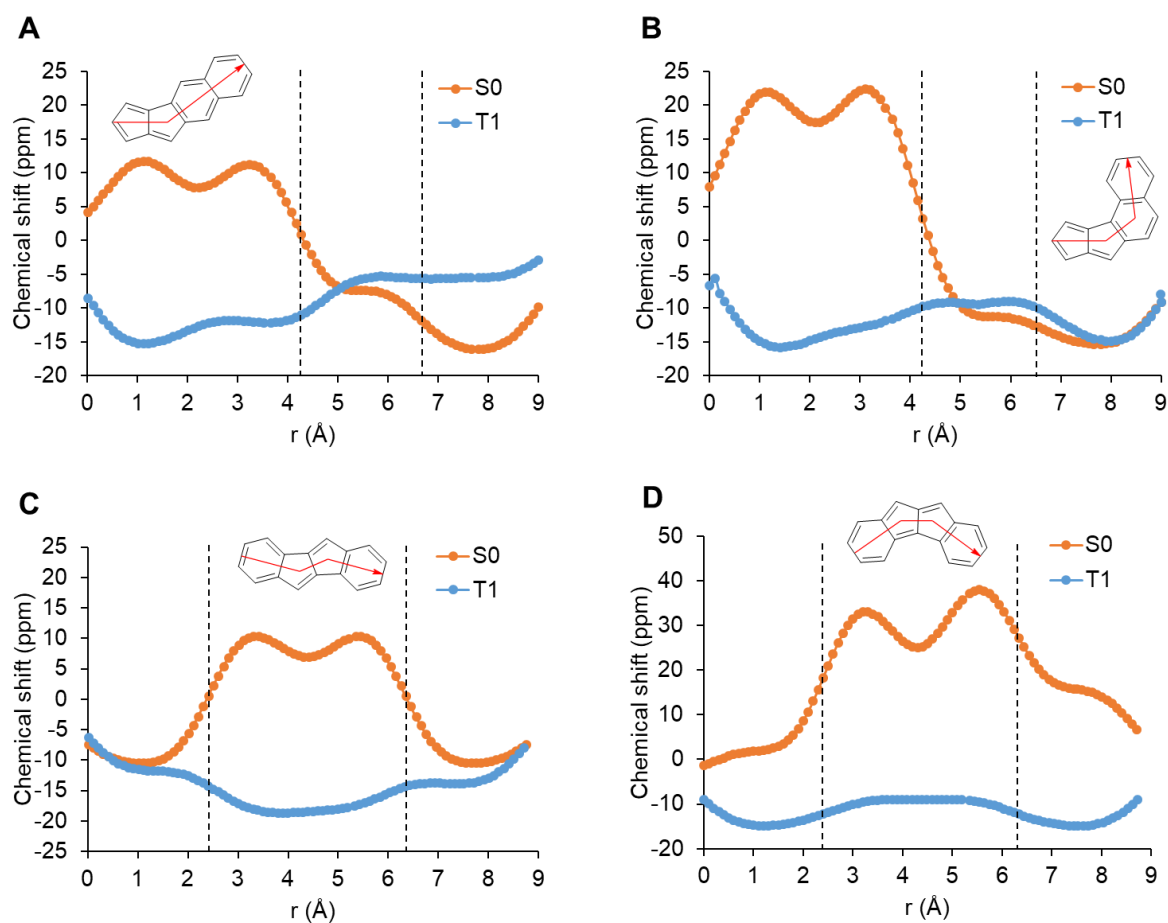


Figure S25. NICS-XY scans of (A) **BENZPENT2**, (B) **BENZPENT4**, (C) **BENZPENT5** and (D) **BENZPENT6** in their S_0 and T_1 states calculated at GIAO/M06-2X/6-311+G(d,p) level.

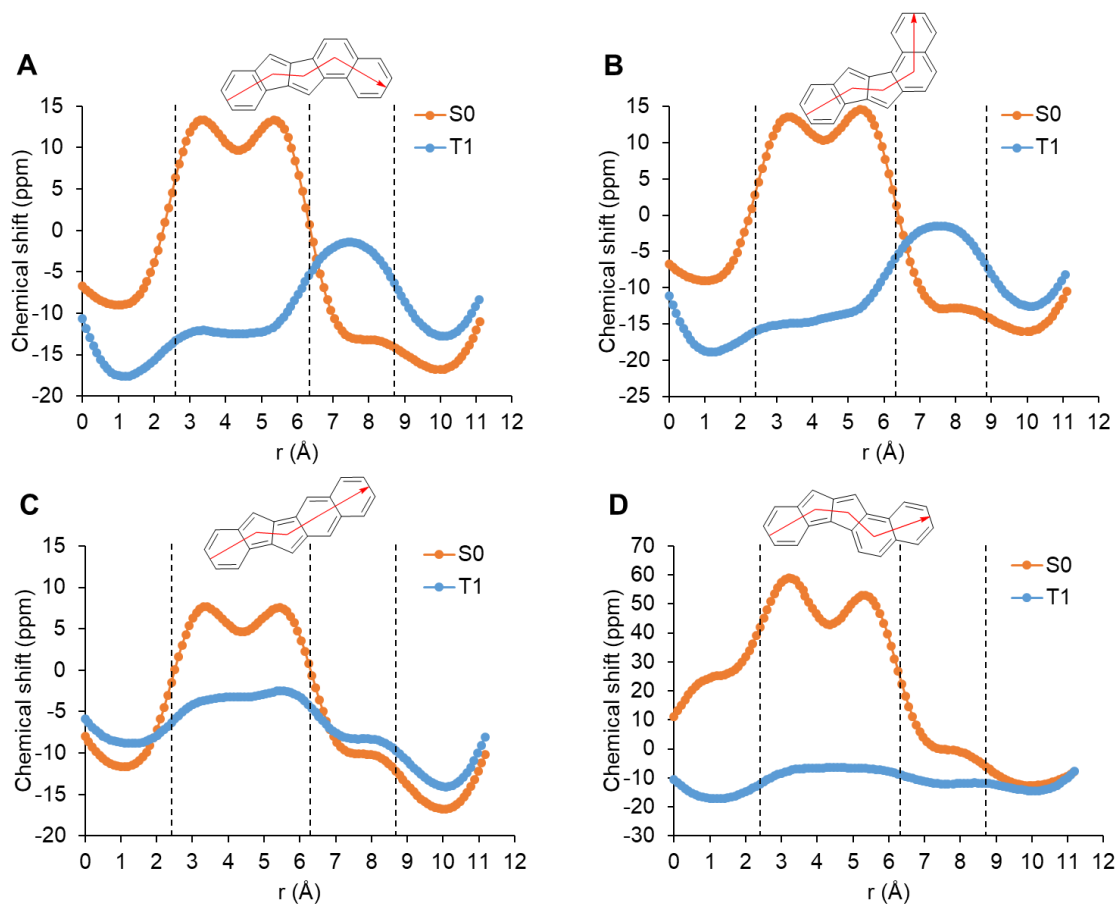


Figure S26. NICS-XY scans of (A) **BENZPENT8**, (B) **BENZPENT9**, (C) **BENZPENT10** and (D) **BENZPENT11** in their S_0 and T_1 states calculated at GIAO/M06-2X/6-311+G(d,p) level.

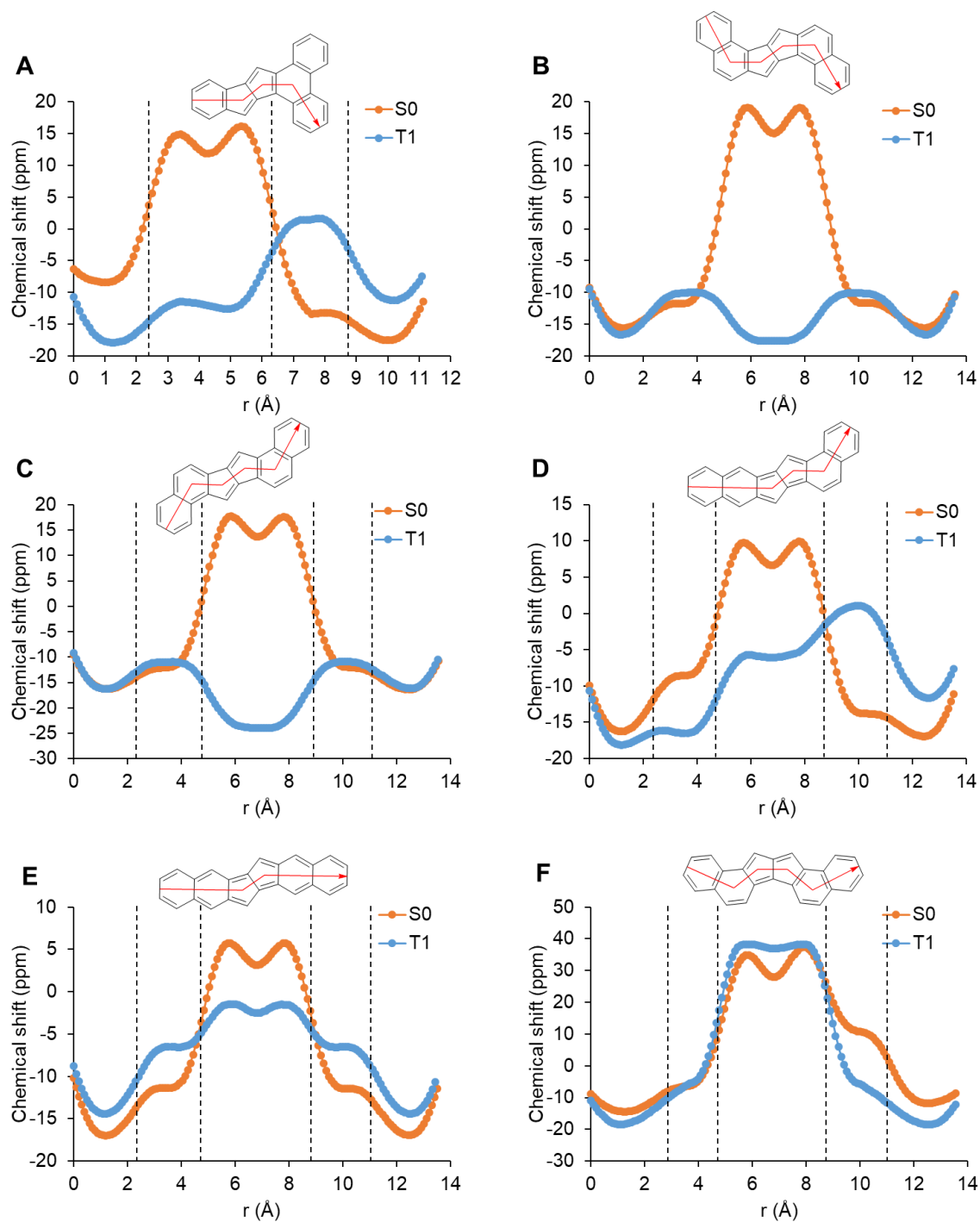


Figure S27. NICS-XY scans of (A) **BENZPENT12**, (B) **BENZPENT13**, (C) **BENZPENT14**, (D) **BENZPENT15**, (E) **BENZPENT16** and (F) **BENZPENT17** in their S₀ and T₁ states calculated at GIAO/M06-2X/6-311+G(d,p) level. **BENZPENT17** is unsymmetric in the S₀ state.

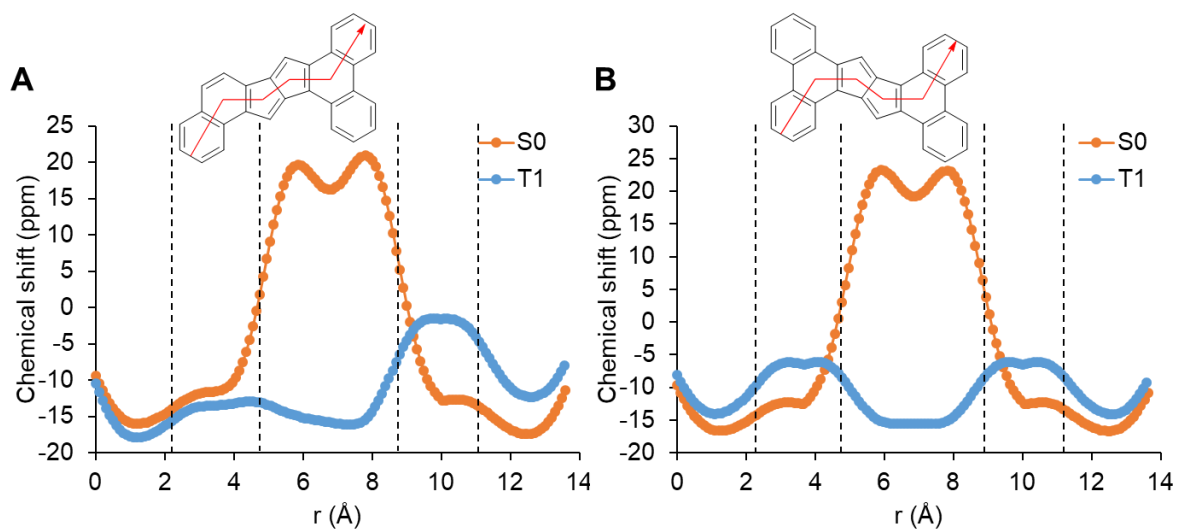


Figure S28. NICS-XY scans of (A) **BENZPENT18** and (B) **BENZPENT19** in their S_0 and T_1 states calculated at GIAO/M06-2X/6-311+G(d,p) level.

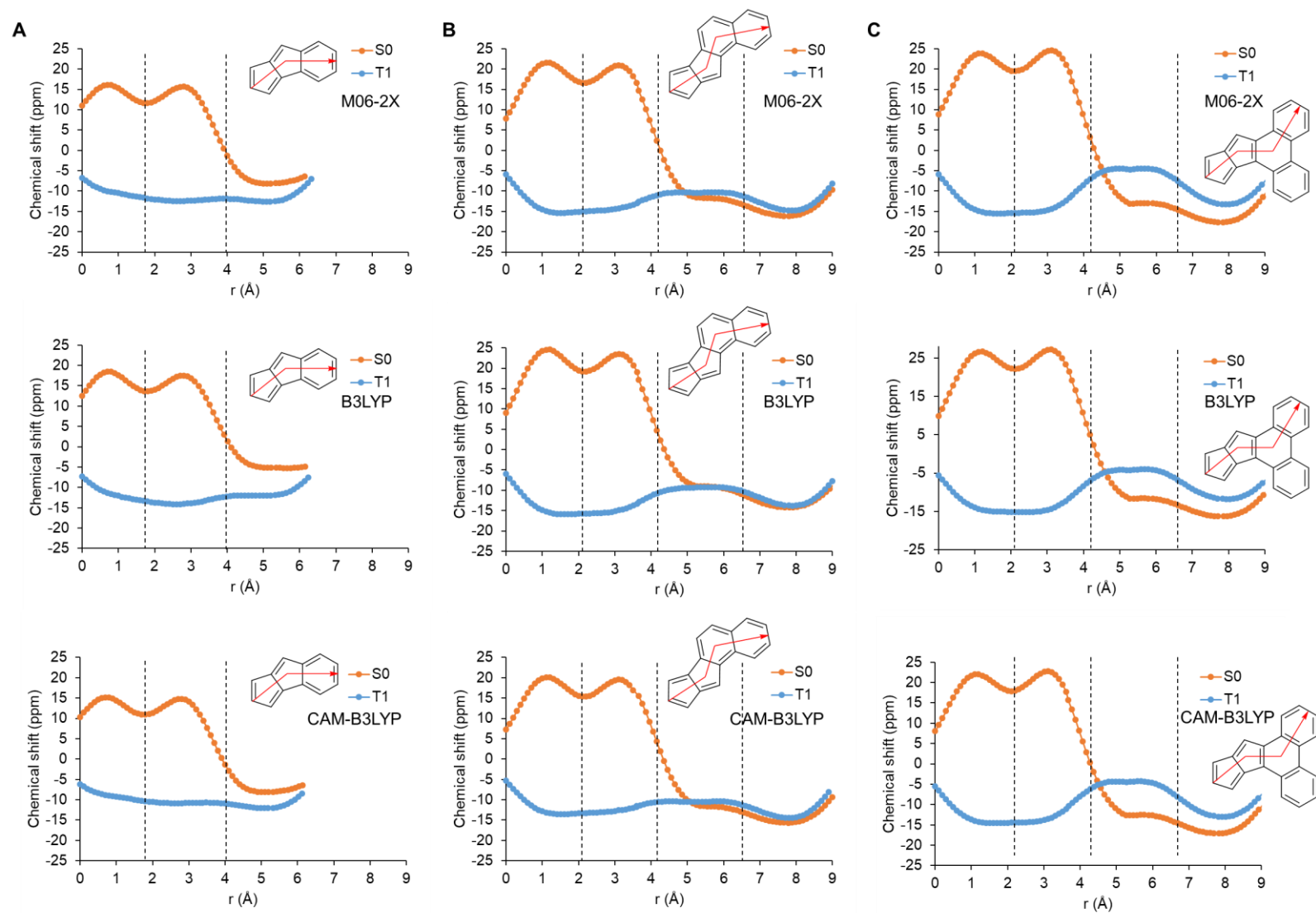


Figure S29. Comparison of NICS-XY scans of (A) **BENZPENT1**, (B) **BENZPENT3** and (C) **BENZPENT7** using M06-2X, B3LYP and CAM-B3LYP.

Full IUPAC names of the benzannulated pentalenes

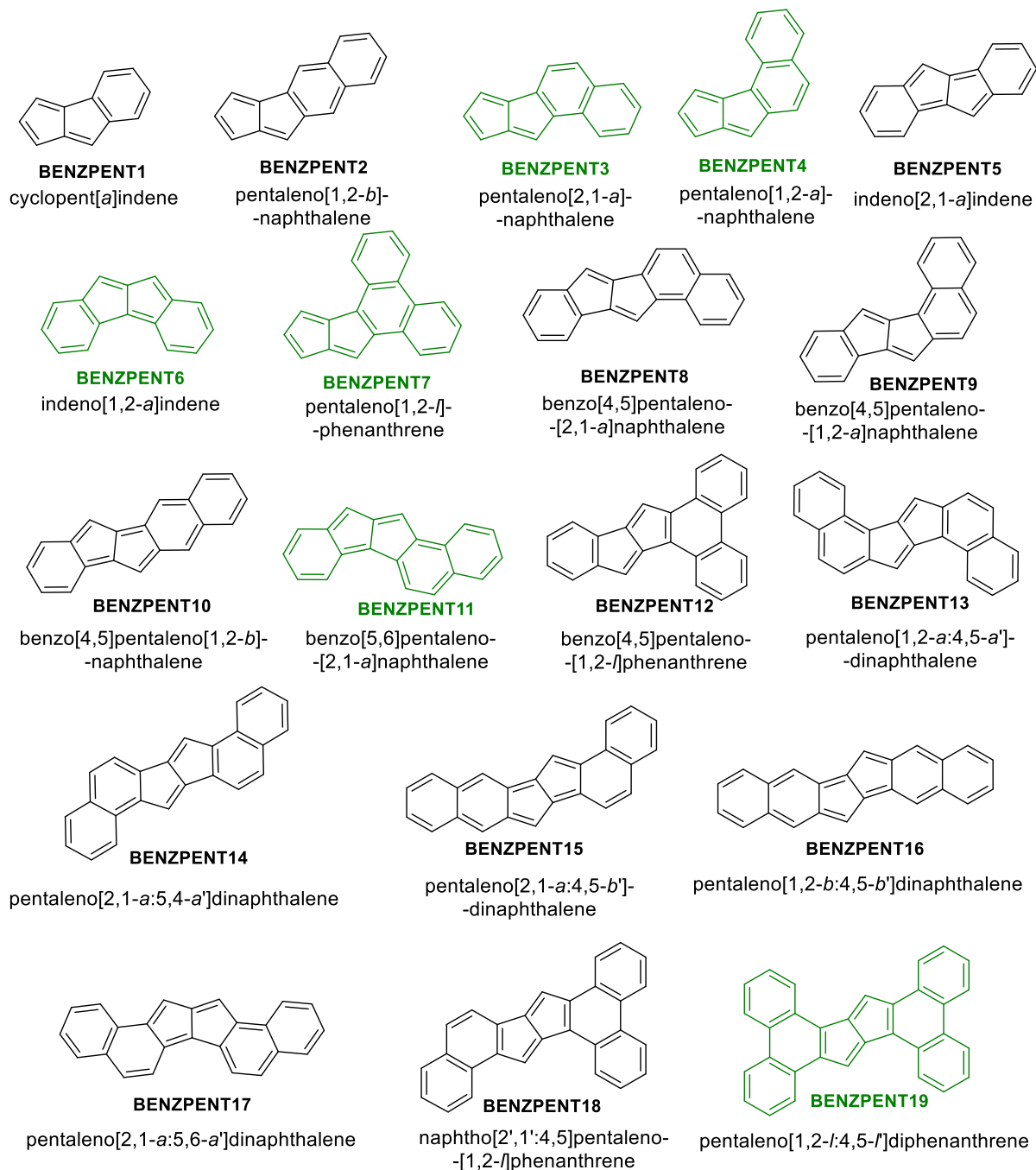


Figure S30. Full IUPAC names of BENZPENTs.

Table S26. Excitation energies and ratios of a few benzannelated CBDs and pentalenes computed at CASPT2/ANO-RCC-VDZP//CASSCF/ ANO-RCC-VDZP level. The subscripts a, v, va and vv stand for adiabatic, vertical, vertical-adiabatic and vertical-vertical.

	$E(T_1)_v$	$E(T_1)_a$	$E(S_1)_v$	$E(S_1)_a$	$E(S_1)_v/E(T_1)_v$	$E(S_1)_v/E(T_1)_a$	$E(S_1)_a/E(T_1)_a$	$E(S_1)_v/E(S_1)_a$	$E(T_1)_v - E(T_1)_a$
BENZCBD1	1.37	2.26	3.48	2.58	1.54	2.54	1.88	1.35	0.90
BENZCBD2	1.00	1.78	2.79	1.99	1.57	2.79	1.99	1.40	0.80
BENZCBD3	1.70	2.58	3.71	3.05	1.44	2.18	1.80	1.22	0.66
BENZCBD4	2.16	2.82	3.70	3.27	1.31	1.71	1.52	1.13	0.43
BENZPENT1	1.08	1.85	2.60	2.23	1.40	2.41	2.07	1.16	0.37

OTHER MOLECULES

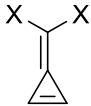
	X = NO₂	X = CN	X = H
	$E(T_1)_a = 3.24$	$E(T_1)_a = 2.85$	$E(T_1)_a = 2.71$
	$E(S_1)_v = 4.17$	$E(S_1)_v = 4.68$	$E(S_1)_v = 4.58$
	$E(T_2)_v = 4.69$	$E(T_2)_v = 5.37$	$E(T_2)_v = 5.23$
	$E(S_1)_v/E(T_1)_a = 1.93$	$E(S_1)_v/E(T_1)_a = 1.64$	$E(S_1)_v/E(T_1)_a = 1.69$
	X = Me	X = OH	X = NH₂
	$E(T_1)_a = 2.13$	$E(T_1)_a = 1.97$	$E(T_1)_a = 1.42$
	$E(S_1)_v = 4.15$	$E(S_1)_v = 4.06$	$E(S_1)_v = 4.39$
	$E(T_2)_v = 5.39$	$E(T_2)_v = 5.15$	$E(T_2)_v = 4.76$
	$E(S_1)_v/E(T_1)_a = 1.94$	$E(S_1)_v/E(T_1)_a = 2.06$	$E(S_1)_v/E(T_1)_a = 3.09$

Figure S31: Electronic excitation energies (eV) of the parent triafulvene and substituted triafulvenes at TD-M06-2X/def2-TZVPD level.

Table S27. The $\Delta E(S_1-T_1)_{va}$ of the parent triafulvene and substituted triafulvenes.

	$\Delta E(S_1-T_1)_{va}$
X = NO₂	0.92
X = CN	1.83
X = H	1.86
X = Me	2.01
X = OH	2.09
X = NH₂	2.97

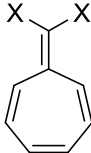
	X = CN	X = H	X = Cl
	$E(T_1)_a = 1.58$	$E(T_1)_a = 1.41$	$E(T_1)_a = 1.40$
	$E(S_1)_v = 3.05$	$E(S_1)_v = 2.95$	$E(S_1)_v = 3.48$
	$E(T_2)_v = 2.47$	$E(T_2)_v = 2.83$	$E(T_2)_v = 2.57$
	$E(S_1)_v/E(T_1)_a = 1.93$	$E(S_1)_v/E(T_1)_a = 2.09$	$E(S_1)_v/E(T_1)_a = 2.49$
	X = F	X = NH₂	
	$E(T_1)_a = 1.30$	$E(T_1)_a = 1.08$	
	$E(S_1)_v = 3.09$	$E(S_1)_v = 2.91$	
	$E(T_2)_v = 2.87$	$E(T_2)_v = 2.83$	
	$E(S_1)_v/E(T_1)_a = 2.37$	$E(S_1)_v/E(T_1)_a = 2.68$	

Figure S32: Electronic excitation energies (eV) of the parent heptafulvene and substituted heptafulvenes at TD-M06-2X/def2-TZVPD.

Table S28. The $\Delta E(S_1-T_1)_{va}$ of the parent heptafulvene and substituted heptafulvenes.

	$\Delta E(S_1-T_1)_{va}$
X = CN	1.47
X = H	1.54
X = Cl	2.08
X = F	1.79
X = NH₂	1.83

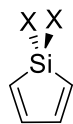
	X, Y = F $E(T_1)_a = 2.02$ $E(S_1)_v = 4.32$ $E(T_2)_v = 4.88$ $E(S_1)_v/E(T_1)_a = 2.14$	X, Y = CF₃ $E(T_1)_a = 2.09$ $E(S_1)_v = 4.37$ $E(T_2)_v = 5.06$ $E(S_1)_v/E(T_1)_a = 2.09$	X, Y = Me $E(T_1)_a = 2.20$ $E(S_1)_v = 4.54$ $E(T_2)_v = 5.08$ $E(S_1)_v/E(T_1)_a = 2.06$	X, Y = H $E(T_1)_a = 2.22$ $E(S_1)_v = 4.56$ $E(T_2)_v = 5.28$ $E(S_1)_v/E(T_1)_a = 2.05$
	X, Y = SiH₃ $E(T_1)_a = 2.33$ $E(S_1)_v = 4.55$ $E(T_2)_v = 4.72$ $E(S_1)_v/E(T_1)_a = 1.96$	X, Y = SiMe₃ $E(T_1)_a = 2.36$ $E(S_1)_v = 4.58$ $E(T_2)_v = 4.37$ $E(S_1)_v/E(T_1)_a = 1.94$	X = CF₃, Y = F $E(T_1)_a = 2.02$ $E(S_1)_v = 4.24$ $E(T_2)_v = 5.00$ $E(S_1)_v/E(T_1)_a = 2.10$	X = CF₃, Y = Me $E(T_1)_a = 2.14$ $E(S_1)_v = 4.43$ $E(T_2)_v = 5.11$ $E(S_1)_v/E(T_1)_a = 2.07$
	X = CF₃, Y = SiH₃ $E(T_1)_a = 2.18$ $E(S_1)_v = 4.41$ $E(T_2)_v = 4.95$ $E(S_1)_v/E(T_1)_a = 2.02$	X = CF₃, Y = SiMe₃ $E(T_1)_a = 2.19$ $E(S_1)_v = 4.43$ $E(T_2)_v = 5.68$ $E(S_1)_v/E(T_1)_a = 2.03$	X = F, Y = Me $E(T_1)_a = 2.06$ $E(S_1)_v = 4.33$ $E(T_2)_v = 4.92$ $E(S_1)_v/E(T_1)_a = 2.10$	X = F, Y = SiH₃ $E(T_1)_a = 2.06$ $E(S_1)_v = 4.20$ $E(T_2)_v = 5.84$ $E(S_1)_v/E(T_1)_a = 2.04$
	X = F, Y = SiMe₃ $E(T_1)_a = 2.07$ $E(S_1)_v = 4.22$ $E(T_2)_v = 5.77$ $E(S_1)_v/E(T_1)_a = 2.03$	X = Me, Y = SiH₃ $E(T_1)_a = 2.25$ $E(S_1)_v = 4.49$ $E(T_2)_v = 4.90$ $E(S_1)_v/E(T_1)_a = 2.00$	X = Me, Y = SiMe₃ $E(T_1)_a = 2.27$ $E(S_1)_v = 4.50$ $E(T_2)_v = 4.62$ $E(S_1)_v/E(T_1)_a = 1.99$	X = SiH₃, Y = SiMe₃ $E(T_1)_a = 2.34$ $E(S_1)_v = 4.57$ $E(T_2)_v = 4.51$ $E(S_1)_v/E(T_1)_a = 1.95$

Figure S33. Electronic excitation energies (eV) of the parent silole and substituted siloles.

Table S29. The $\Delta E(S_1-T_1)$ of the parent silole and substituted siloles.

	$\Delta E(S_1-T_1)_{va}$	$\Delta E(S_1-T_1)_{vv}$
X = H	2.34	1.65
X, Y = F	2.29	1.60
X = F Y = Me	2.27	1.58
X = F Y = SiH₃	2.14	1.44
X = F Y = SiMe₃	2.14	1.44
X, Y = CF₃	2.27	1.59
X = CF₃ Y = F	2.22	1.53
X = CF₃ Y = Me	2.29	1.61
X = CF₃ Y = SiH₃	2.23	1.55
X = CF₃ Y = SiMe₃	2.25	1.56
X, Y = Me	2.33	1.65
X = Me Y = SiH₃	2.24	1.56
X = Me Y = SiMe₃	2.24	1.57
X, Y = SiH₃	2.22	1.55
X = SiH₃ Y = SiMe₃	2.23	1.56
X, Y = SiMe₃	2.22	1.57

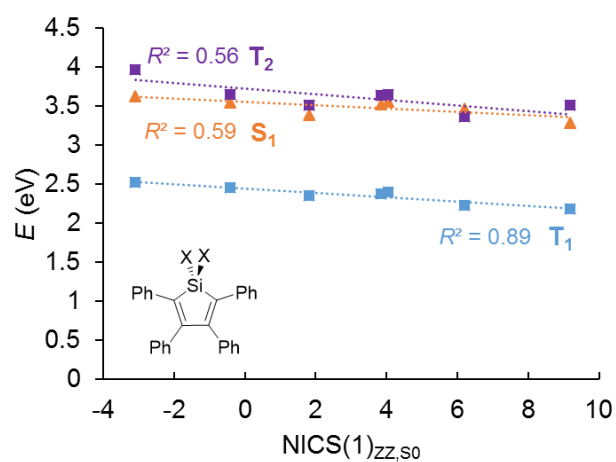


Figure S34. 1,1-Disubstituted tetraphenylsilole with X = H, Me, CF₃, F, SiH₃ and SiMe₃.

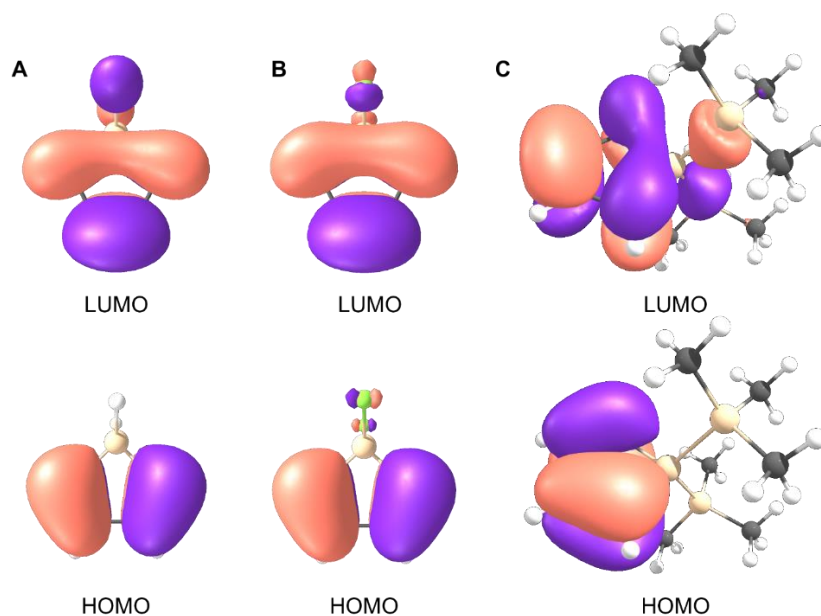


Figure S35. HOMO and LUMO and HOMO of the siloles with (A) X = H, (B) X = F and (C) X = SiMe₃ obtained at M06-2X/6-311+G(d,p) level.

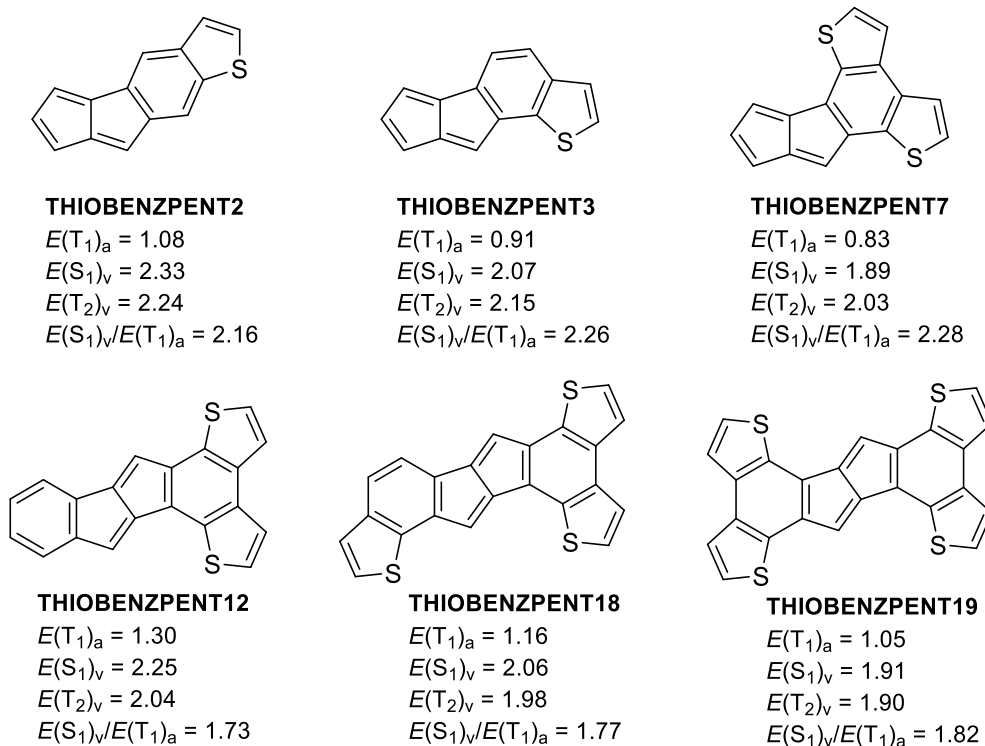


Figure S36. Electronic excitation energies (eV) of thieno-annulated benzopentalenes (THIOBENZPENT).

Table S30. The $\Delta E(S_1-T_1)_{va}$ of thieno-annulated benzopentalenes (THIOBENZPENT).

	$\Delta E(S_1-T_1)_{va}$
THIOBENZPENT2	1.26
THIOBENZPENT3	1.15
THIOBENZPENT7	1.06
THIOBENZPENT12	0.95
THIOBENZPENT18	0.90
THIOBENZPENT19	0.86

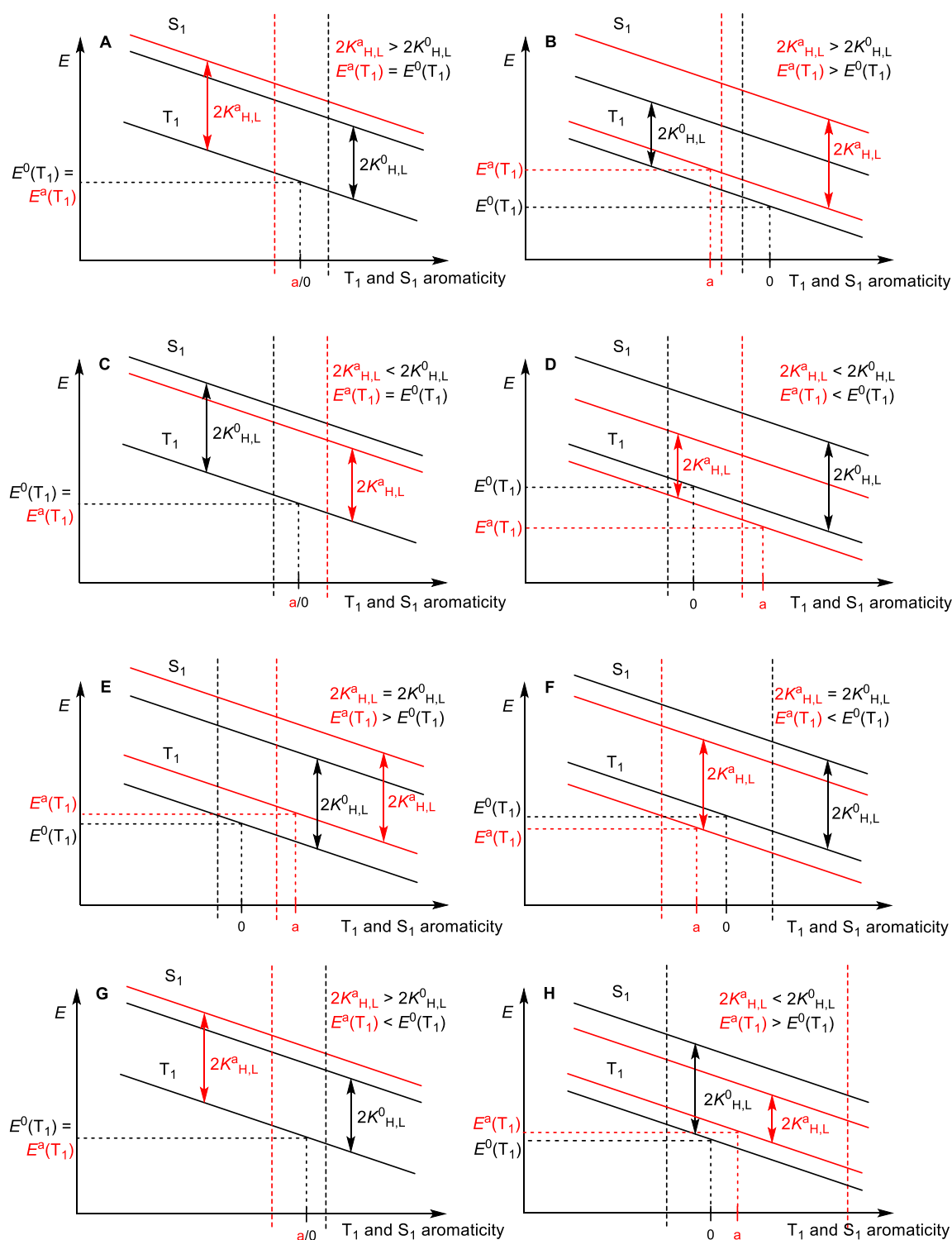


Figure S37: Additional schematic drawings of the changes in $E(T_1)$ and $E(S_1)$ as functions of increased T_1 and S_1 aromatic character for a compound class. Given certain relationships between the parent compound in a certain compound class “a” and the parent compound in the reference compound class “0”, the following will be the situation:

A: If “a” and “0” have the same $E(T_1)$ but $2K_{H,L}$ of “a” is higher than $2K_{H,L}$ of “0”, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at less T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.

- B:** If $E(T_1)$ of “a” is higher than $E(T_1)$ of “0” and $2K_{H,L}$ of “a” is higher than $2K_{H,L}$ of “0”, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at less T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.
- C:** If “a” and “0” have the same $E(T_1)$ but $2K_{H,L}$ of “a” is lower than $2K_{H,L}$ of “0”, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at more T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.
- D:** If $E(T_1)$ of “a” is lower than $E(T_1)$ of “0” and $2K_{H,L}$ of “a” is lower than $2K_{H,L}$ of “0”, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at more T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.
- E:** If $E(T_1)$ of “a” is higher than $E(T_1)$ of “0”, and “a” and “0” have the same $2K_{H,L}$, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at more T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.
- F:** If $E(T_1)$ of “a” is lower than $E(T_1)$ of “0”, and “a” and “0” have the same $2K_{H,L}$, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at less T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.
- G:** If $E(T_1)$ of “a” is lower than $E(T_1)$ of “0” and $2K_{H,L}$ of “a” is higher than $2K_{H,L}$ of “0”, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at less T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.
- H:** If $E(T_1)$ of “a” is higher than $E(T_1)$ of “0” and $2K_{H,L}$ of “a” is lower than $2K_{H,L}$ of “0”, then the singlet fission threshold $2E(T_1) = E(S_1)$ will be placed at more T_1 aromatic compounds for the compound class “a” than for the reference compound class “0”.

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