Supporting Information for

The low lying double-exciton state of conjugated diradicals: assessment of TDUDFT and spin-flip TDDFT predictions.

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Table S1 Absolute energies of the CS and BS equilibrium structures for the systems investigated. The functional used in the calculations is the B3LYP, the basis set is 6-31G*.

molecule	*CS B3LYP*	*BS B3LYP*
NZ	-1383,936580	-1383,942002
DIPh	-1774,623756	-1774,629582
PT	-1381,599172	-1381,606370
SOZ	-1765,093753	-1765,111034

Table S2 Overlap (*S*) between BS frontier molecular orbitals H_α, H_β , L_α, L_β obtained from UB3LYP/6-31G* calculations for the singlet open-shell configuration, along with the diradical character computed at PUB3LYP level. All data are computed employing the BS UB3LYP/6-31G* optimized geometry.

	y_0 *PUB3LYP*	$S(H_\alpha,H_\beta)$	$S(L_\alpha,L_\beta)$	$S(H_\alpha,L_\beta)$ and $S(H_\beta,L_\alpha)$
NZ	0.23	0.45	-0.50	0.87
DIPh	0.28	0.40	-0.46	0.86
PT	0.36	0.33	-0.37	0.92
SOZ	0.66	0.15	-0.18	0.97

Table S3 Diradical character y_0 computed at PUB3LYP level and orbital rotation angle θ deduced from HOMO and LUMO BS orbitals decomposition.

	y_0 *PUB3LYP*	θ *(HOMO)*	θ *(LUMO)*
2TIO	0.10[1]	28.3	25.8
QDTBDT	0.14[1]	29.5	27.1
NZ	0.23	31.8	30.7
BISPHE	0.26[1]	32.9	31.8
DIPh	0.28	34.9	31.8
DFB	0.30[1]	38.7	32.9
FP	0.34[1]	37.7	33.9
PT	0.36	35.9	33.9
TPQ	0.42[1]	41.4	35.9
SHZ	0.52[1]	38.7	37.8
SOZ	0.66	41.4	40.5
QANTHENE	0.71[1]	43.3	41.4

[1] From ref. [1].

Table S4 Computed TD-UB3LYP excitation energies, spin contamination S^2, wavefunction composition, oscillator strength *f* of the double-exciton state *(H,H→L,L)* and the available experimental excitation energies for the systems investigated.

Excited state character →		*(H,H→L,L)*[a]				
	y_0 *PUB3LYP*	*E(eV)*	S^2	*wf*	*f*	*Exp/eV*
NZ	0.23	1.22	0.63	0.68 Hα →Lα; 0.68 Hβ →Lβ	0.000	1.39[b]
DIPh	0.28	1.21	0.49	0.68 Hα →Lα; 0.68 Hβ →Lβ	0.000	1.18[c]
PT	0.36	1.13	0.36	0.70 Hα →Lα; 0.70 Hβ →Lβ	0.000	1.23[d]
SOZ	0.66	1.41	0.74	0.47 Hα →Lα; 0.47 Hβ →Lβ	0.000	1.07[e]

[a] Geometry optimized at UB3LYP/6-31G* (BS) level of theory. [b] Measured in DCM, from ref. [2]. [c] Measured in DCM, from ref. [3]. [d] Measured in DCM, from ref. [4]. [e] Measured in CCl_4, from ref. [5].

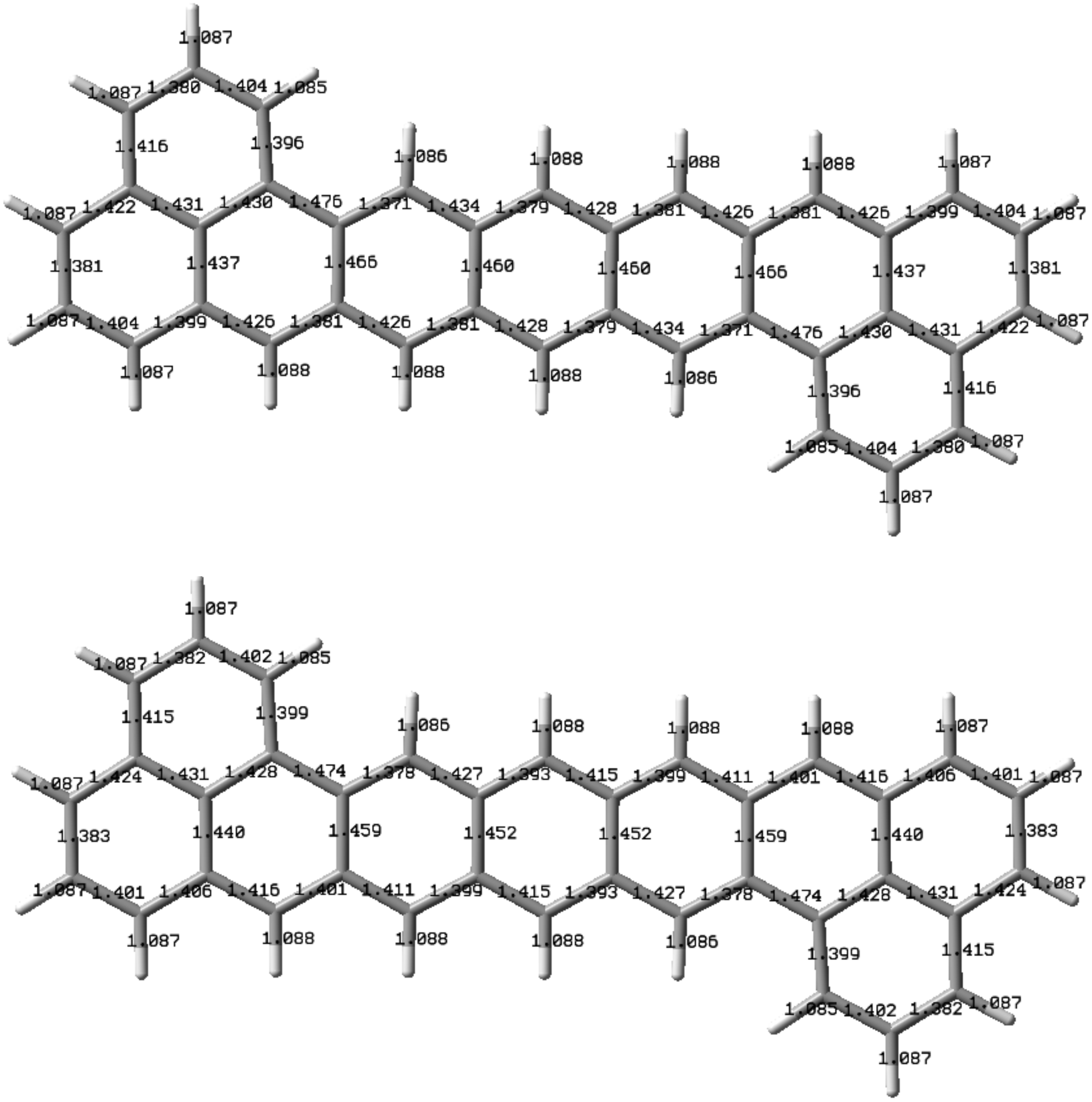

Figure S1. NZ: (top) CS and (bottom) BS equilibrium structures from B3LYP/6-31G* calculations.

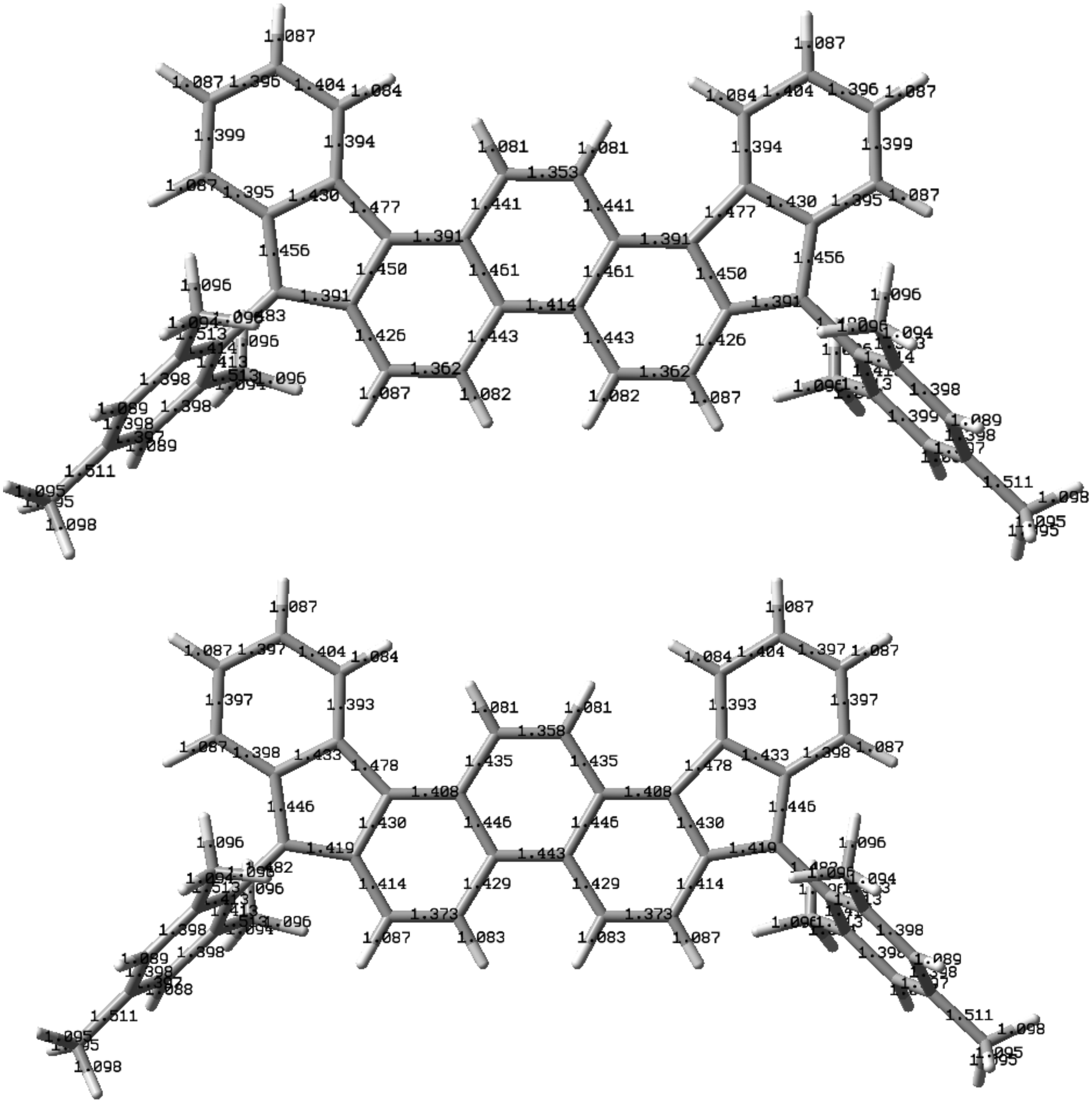

Figure S2. DIPh: (top) CS and (bottom) BS equilibrium structures from B3LYP/6-31G* calculations.

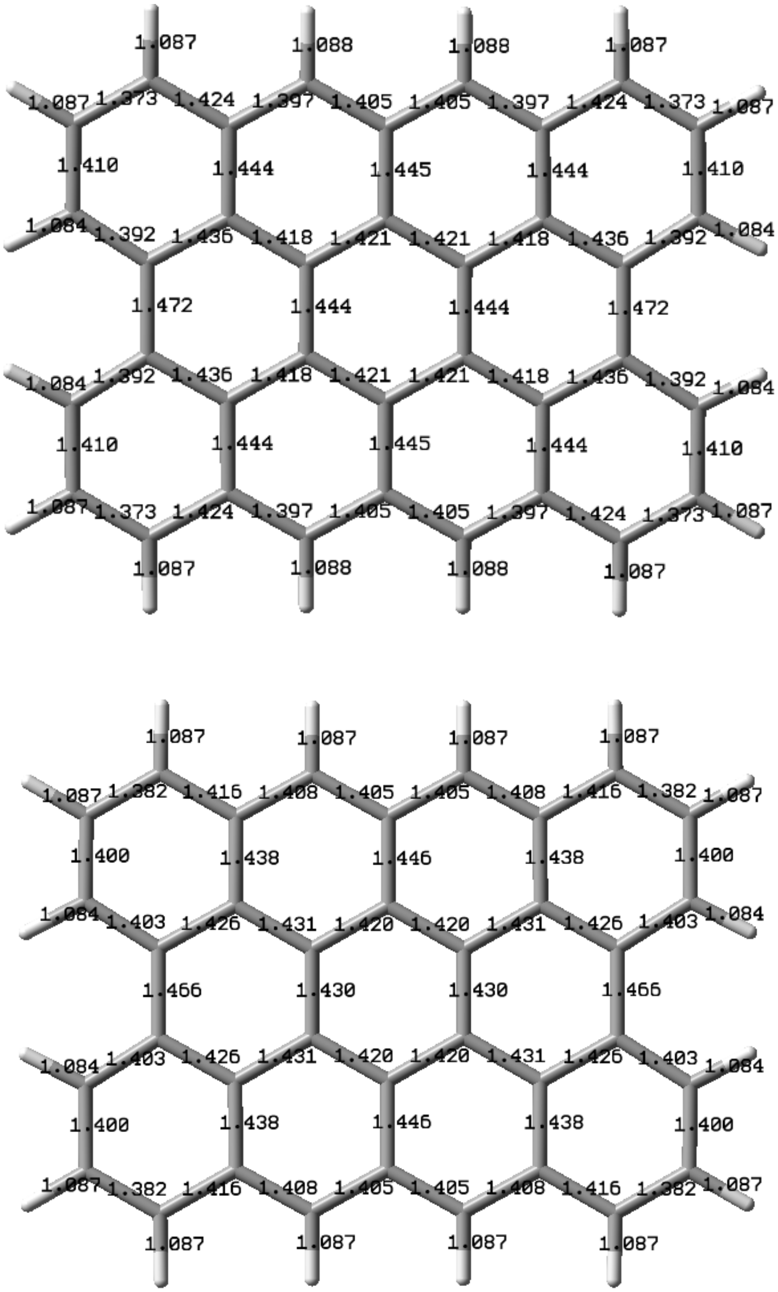

Figure S3. PT: (top) CS and (bottom) BS equilibrium structures from B3LYP/6-31G* calculations.

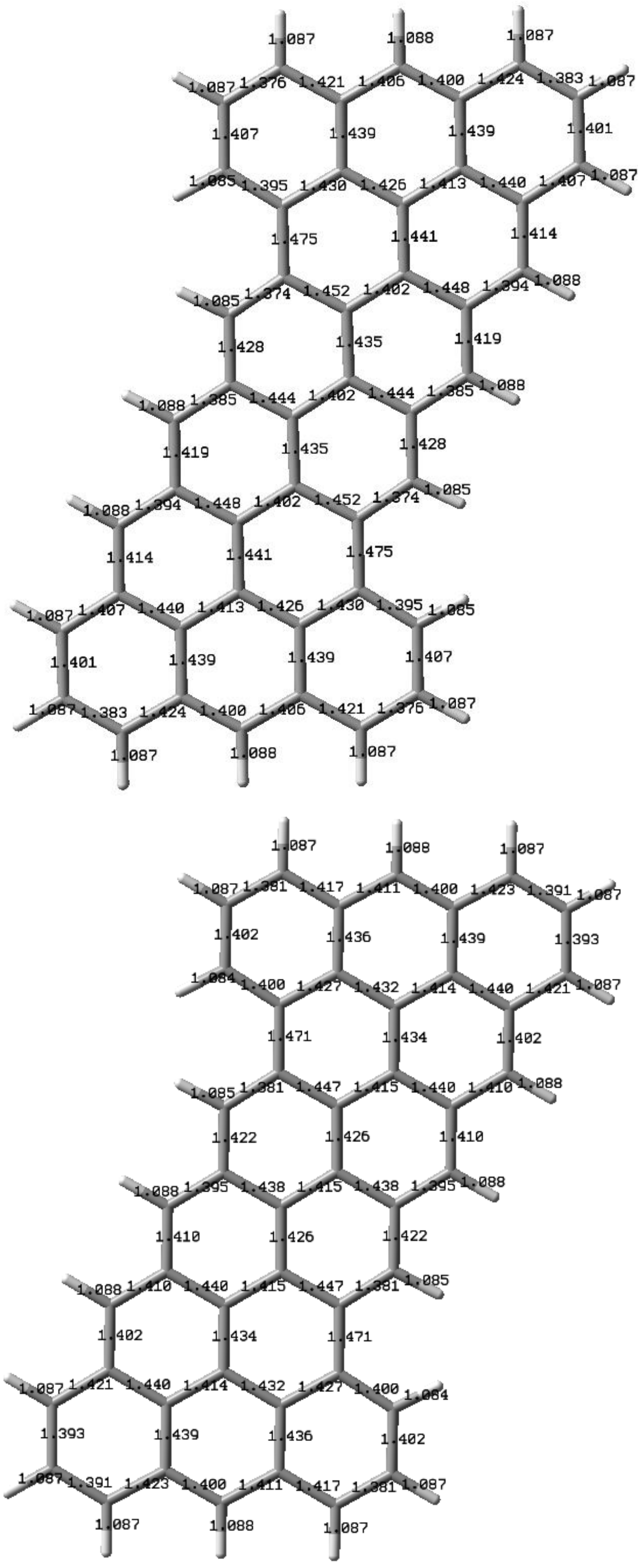

Figure S4. SOZ: (top) CS and (bottom) BS equilibrium structures from B3LYP/6-31G* calculations.

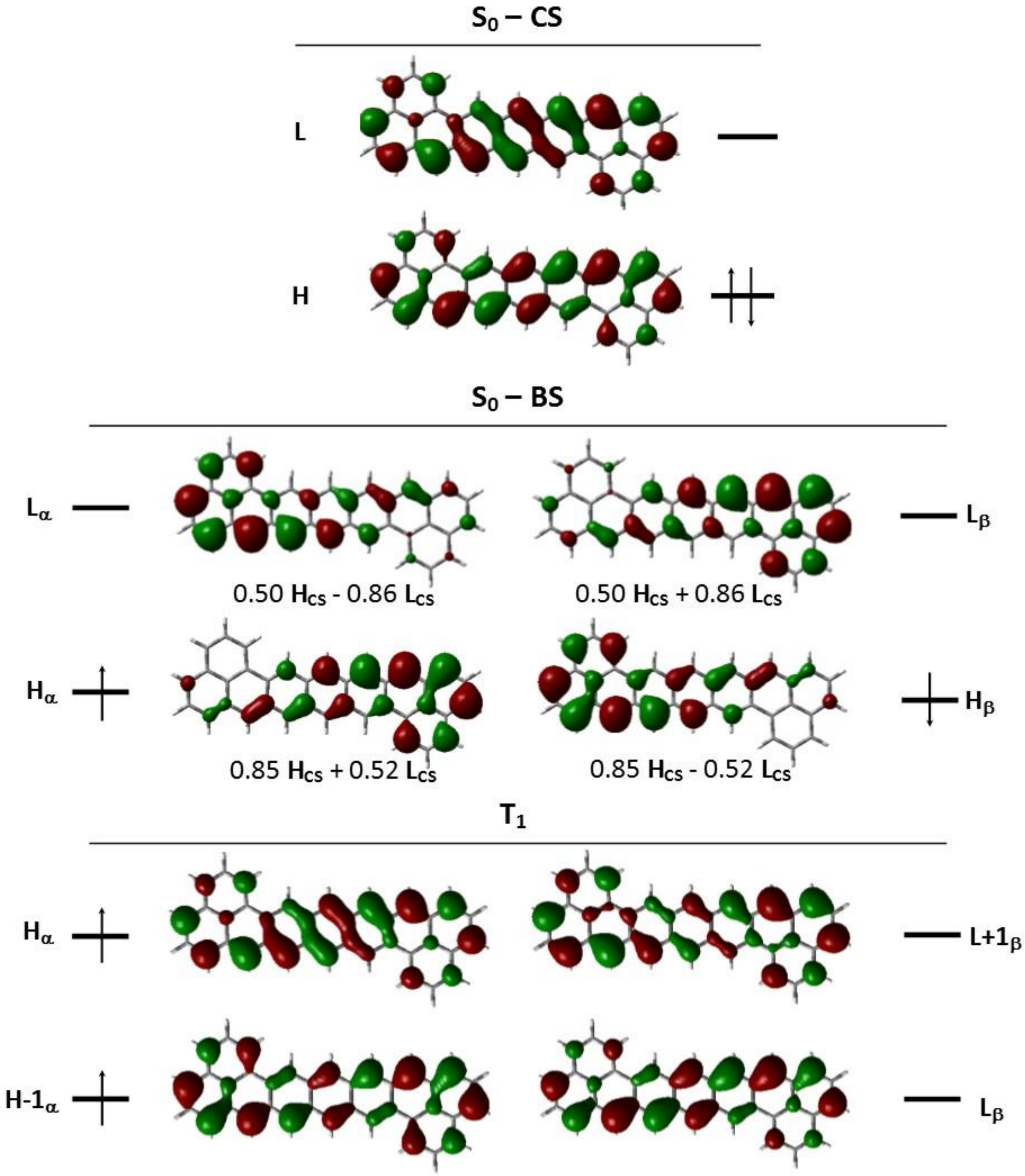

Figure S5. Frontier molecular orbitals of NZ computed with (top) a CS singlet reference configuration, (middle) a BS singlet open-shell configuration and (bottom) a triplet configuration, at the optimized BS UB3LYP geometry of the singlet ground state ($y_0(PUB3LYP) = 0.23$). Each localized orbital (BS) is also expressed as a linear combination of the delocalized (CS) orbitals.

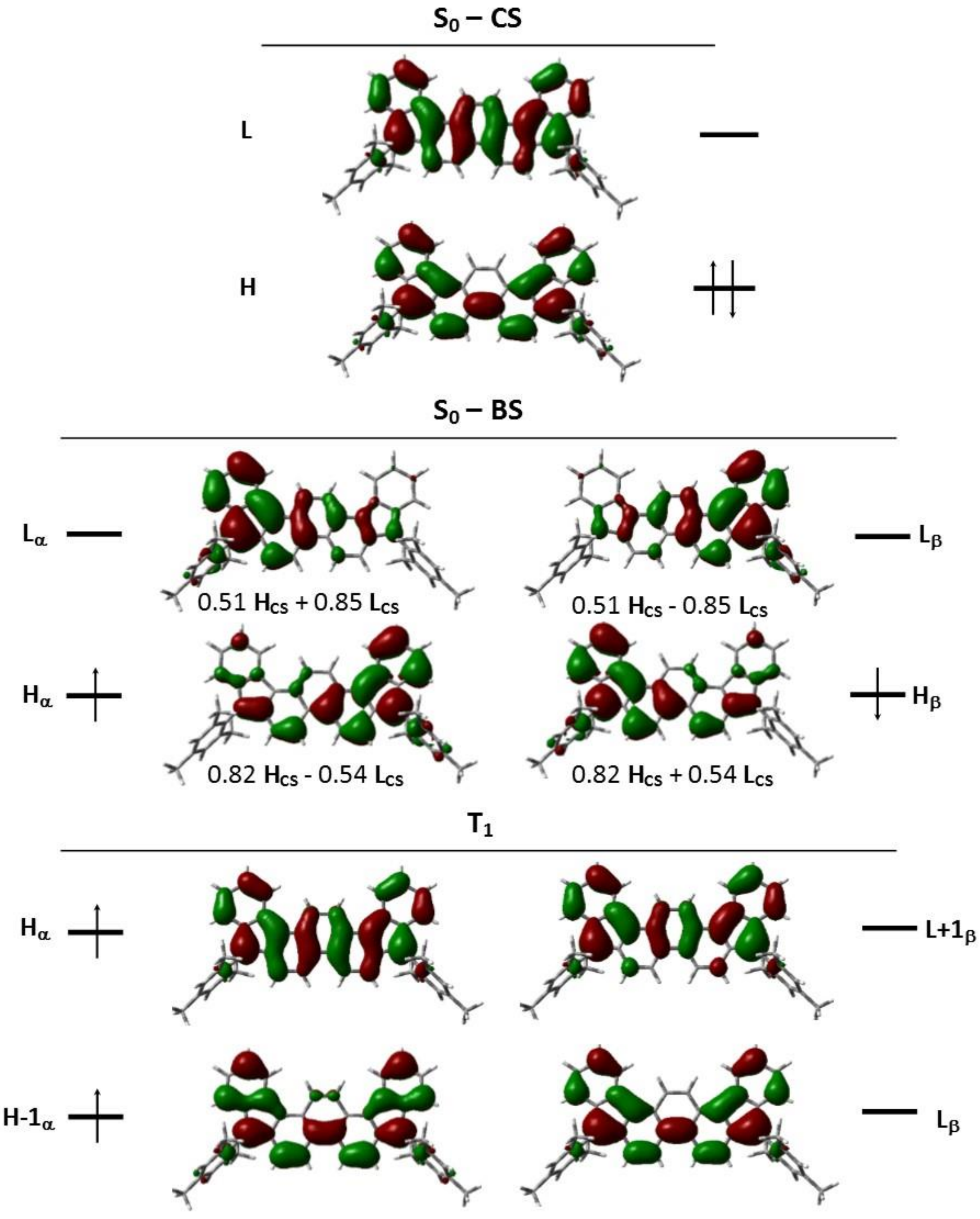

Figure S6. Frontier molecular orbitals of DIPh computed with (top) a CS singlet reference configuration, (middle) a BS singlet open-shell configuration and (bottom) a triplet configuration, at the optimized BS UB3LYP geometry of the singlet ground state ($y_0(PUB3LYP) = 0.28$). Each localized orbital (BS) is also expressed as a linear combination of the delocalized (CS) orbitals.

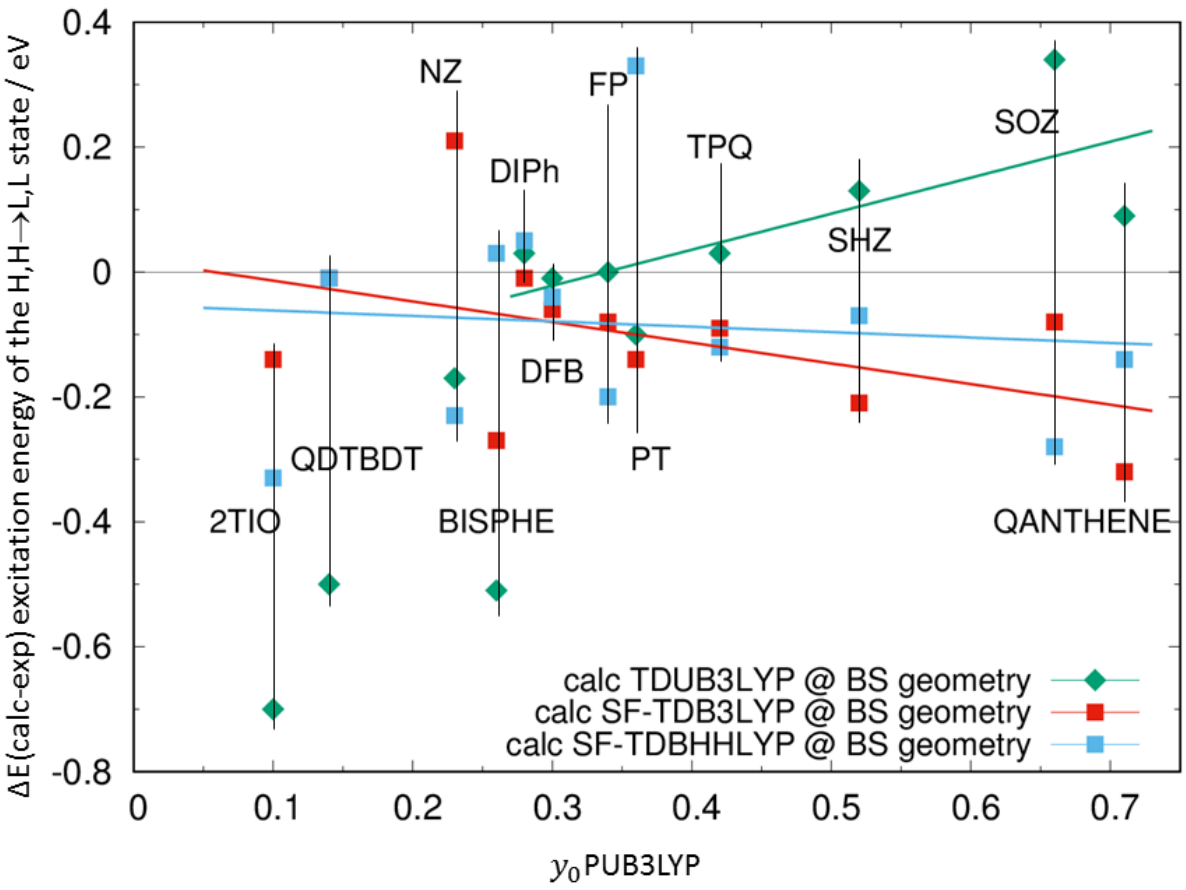

Figure S7. Difference between computed and observed excitation energy of the double exciton (H,H→L,L) state versus the computed y_0 at PUB3LYP level: (red squares) SF-TDB3LYP at BS B3LYP geometry; (blue squares) SF-TDBHHLYP at BS B3LYP geometry; (green diamonds) TDUB3LYP at the same geometry. The lines in the same colours are linear fittings of the computed data. Vertical bars indicate the compound to which computed data correspond. Some data are taken from ref. [1].

References

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