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. Yet, M06-2X was found to perform similarly, and we used this functional as we showed earlier that it gives good T1 state geometries for substituted fulvenes when compared to the T1 state geometries calculated with CASPT2. We first used the computational scheme derived by Zeng, Hoffmann, and Ananth which gives the correct ordering of the T1, S1, and T2 states of pentacene. This approach uses adiabatic excitations to the T1 state and vertical excitations to the S1 (T2) states from the S0 (T1) optimized structures. Additionally, the vertical excitations to the T1 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 \( \pi \)-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 | \( E(T_1)^a \) | \( S_1^b \) | \( T_2^b \) | \( E(S_1)/E(T_1) \) | \( E(T_2)/E(S_1) \) |
|----------|----------------|------------|------------|-----------------|-----------------|
| CBD      | 0.51 (0.49)    | 2.70 (2.94)| 4.69 (5.27)| 5.29 (6.00)     | 1.66 (1.79)     |
| Benzene  | 4.49 (3.96)    | 5.57 (5.09)| 6.64 (6.10)| 1.24 (1.29)     | 1.19 (1.20)     |
| Pentacene| 0.98 (0.86)    | 2.28 (2.30)| 2.38 (>2.00)| 2.33 (2.67)     | 1.04 (0.87)     |
| DPB      | 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 $E(T_1)v$, $E(T_2)v$, $E(S_1)$ 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.

| X=H | Y = H | 2.53 | 1.72 | 3.64 | 3.20 | 2.12 | 0.88 | 1.86 |
|-----|-------|------|------|------|------|------|------|------|
| X = BF₂ | Y = BF₂ | 2.22 | 1.39 | 3.31 | 2.63 | 2.39 | 0.79 | 1.89 |
| Y = BH₂ | 2.03 | 1.13 | 3.23 | 3.39 | 2.85 | 1.05 | 2.99 |
| Y = CF₃ | 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 = NH₂ | REARRANGED |
| Y = NMe₂ | REARRANGED |
| Y = NO₂ | REARRANGED |
| 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 = SiH₃ | 2.04 | 1.21 | 2.91 | 2.52 | 2.41 | 0.87 | 2.09 |
| X = BH₂ | Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
| Y = BF₂ | REARRANGED |
| Y = CF₃ | T₁ excitation is different to that of the parent fulvene |
| Y = Cl | 2.43 | 1.28 | 3.12 | 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 = NH₂ | REARRANGED |
| Y = NMe₂ | REARRANGED |
| Y = NO₂ | REARRANGED |
| Y = OH | S₁ 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 = SiH₃ | REARRANGED |
| X = Cl | Y = BF₂ | 2.38 | 1.73 | 3.56 | 2.78 | 2.06 | 0.78 | 1.61 |
| Y = BH₂ | 2.21 | 1.59 | 3.47 | 2.77 | 2.18 | 0.80 | 1.74 |
| Y = CF₃ | 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 |
| X   | Y     | X = CN | Y = BF₂ | Y = BH₂ | Y = CF₃ | Y = Cl  | Y = CN | Y = F  | Y = Me  | Y = NH₂ | Y = NH₂  |
|-----|-------|--------|---------|---------|---------|--------|--------|--------|---------|---------|----------|
|     |       |        |         |         |         |        |        |        |         |         |          |
|     |       |        |         |         |         |        |        |        |         |         | T₀ ground state |
| Y = NH₂ | 1.62  | 0.46  | 2.42   | 3.29   | 3.81   | 1.36   | 5.17   |
| Y = NMe₂ | 1.81  | 0.97  | 2.56   | 3.38   | 2.65   | 1.32   | 3.50   |
| Y = NO₂ | 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 = SiH₃| 2.45  | 1.72  | 3.47   | 2.93   | 2.02   | 0.84   | 1.70   |
| X = CN | Y = BF₂ | 2.06  | 1.31  | 3.01   | 2.45   | 2.29   | 0.81   | 1.86   |
| Y = BH₂ | 1.94  | 1.24  | 2.98   | 3.04   | 2.40   | 1.02   | 2.45   |
| Y = CF₃ | 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 = NH₂ | 1.03  | 0.21  | 1.63   | 3.41   | 7.77   | 2.10   | 16.29  |
| Y = NMe₂ | 1.99  | 1.25  | 2.91   | 2.41   | 2.32   | 0.83   | 1.93   |
| Y = NO₂ | 1.19  | 0.45  | 1.89   | 2.84   | 4.20   | 1.50   | 6.30   |
| Y = OH  | 1.22  | 0.53  | 1.90   | 2.86   | 3.59   | 1.50   | 5.40   |
| Y = OMe | 0.98  | 0.38  | 1.62   | 2.70   | 4.24   | 1.67   | 7.08   |
| Y = SH  | 1.93  | 1.23  | 2.73   | 2.54   | 2.22   | 0.93   | 2.06   |
| Y = SiH₃ | 2.62  | 2.03  | 4.02   | 3.09   | 1.98   | 0.77   | 1.52   |
| Y = BF₂ | 2.25  | 1.82  | 3.78   | 2.85   | 2.08   | 0.76   | 1.57   |
| Y = BH₂ | 2.88  | 2.12  | 4.18   | 3.36   | 1.97   | 0.80   | 1.58   |
| Y = CF₃ | 2.43  | 1.66  | 3.51   | 3.27   | 2.11   | 0.93   | 1.96   |
| Y = Cl  | 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 = NH₂ | 2.00  | 0.93  | 2.94   | 3.31   | 3.17   | 1.12   | 3.57   |
| Y = NMe₂ | 2.18  | 1.23  | 3.07   | 3.39   | 2.49   | 1.10   | 2.74   |
| Y = NO₂ | 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 = SiH₃ | 2.73  | 2.01  | 3.94   | 3.13   | 1.96   | 0.79   | 1.55   |
| X = H  | Y = BF₂ | 2.43  | 1.83  | 3.76   | 2.85   | 2.06   | 0.76   | 1.56   |
| Y = BH₂ | LUMO primarily localized on the Y substituents |
| Y = CF₃ | 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   | 0.44   | 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 = NH₂ | 1.74  | 0.87  | 2.59   | 3.70   | 2.98   | 1.43   | 4.27   |
| Y = NMe₂ | 1.93  | 1.09  | 2.76   | 3.65   | 2.52   | 1.32   | 3.34   |

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| X = NO₂ | Y = NH₂ | REARRANGED |
|---------|---------|------------|
| Y = OH  | 2.31    | 1.70       |
| Y = OMe | 0.76    | 1.59       |
| Y = SH  | 2.06    | 1.22       |
| Y = SiH₃| 2.51    | 1.78       |
| Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
| Y = NH₂ | LUMO primarily localized on the Y substituents |
| Y = SiH₃| Not a clear HOMO-to-LUMO excitation |

| X = Me | Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
|--------|---------|---------------------------------------------------------|
| Y = BH₃| LUMO primarily localized on the Y substituents |
| X = NH₂| REARRANGED |
| Y = BF₂| REARRANGED |
| X = CF₃| Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = Cl | 2.30    | 1.52       |
| Y = CN | 2.31    | 1.75       |
| Y = F  | 2.38    | 1.53       |
| Y = Me | 2.46    | 1.62       |
| Y = NH₂| 1.96    | 0.99       |
| Y = NMe₂| 2.13    | 1.18       |
| Y = NO₂| Not a clear HOMO-to-LUMO excitation |
| Y = OH | 2.14    | 1.29       |
| Y = OMe| 2.24    | 1.49       |
| Y = SH | 1.99    | 1.29       |
| Y = SiH₃| 2.64    | 1.92       |

| X = NMe₂| Y = BF₂ | REARRANGED |
|--------|---------|------------|
| Y = BH₂| REARRANGED |
| X = CF₃| Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = Cl | 2.97    | 2.26       |
| Y = CN | 3.01    | 2.00       |
| Y = F  | 2.92    | 2.25       |
| Y = Me | 2.78    | 1.97       |
| Y = NH₂| 2.37    | 1.23       |
| Y = NMe₂| 2.56    | 1.69       |
| Y = NO₂| Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = OH | T₁ excitation is different to that of the parent fulvene |

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| X = NO₂ | Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
| --- | --- | --- |
| Y = SH | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = SiH₃ | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| X = NO₂ | Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
| Y = BF₂ | 2.11 | 0.67 | 3.06 | 3.08 | 4.57 | 1.01 | 4.60 |
| Y = BH₂ | REARRANGED |
| Y = CF₃ | 2.24 | 1.30 | 2.22 | 2.43 | 2.48 | 0.72 | 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 = NMe₂ | Not a clear HOMO-to-LUMO excitation |
| Y = NO₂ | 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 | 6.07 |
| Y = SH | 1.50 | 0.45 | 2.19 | 2.82 | 4.84 | 1.29 | 6.23 |
| Y = SiH₃ | 2.00 | 1.18 | 2.81 | 2.76 | 2.39 | 0.98 | 2.34 |
| X = OH | Y = BF₂ | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = BH₂ | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = CF₃ | T₁ 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 = NH₂ | 1.98 | 1.06 | 2.87 | 3.50 | 2.70 | 1.22 | 3.30 |
| Y = NMe₂ | HOMO is of a different character compared to that of the parent fulvene |
| Y = NO₂ | 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 = SiH₃ | LUMO primarily localized on the Y substituents |
| Y=H | Y = BF₂ | 1.91 | 1.13 | 2.75 | 2.87 | 2.43 | 1.04 | 2.54 |
| Y = BH₂ | 1.88 | 1.06 | 2.64 | 2.60 | 2.49 | 0.99 | 2.45 |
| Y = CF₃ | 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 = NH₂ | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = NMe₂ | T₁ excitation is different to that of the parent fulvene |
| Y = NO₂ | 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 |
| X=SiH₃ | Y | 2.30 | 1.46 | 3.27 | 2.90 | 2.24 | 0.89 | 1.99 |
| X=BF₂ | Y | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| X=BF₂ | Y | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| X=CF₃ | Y | T₁ excitation is different to that of the parent fulvene |
| X=Cl | Y | T₁ excitation is different to that of the parent fulvene |
| X=CN | Y | T₁ excitation is different to that of the parent fulvene |
| X=F | Y | 2.33 | 1.46 | 3.23 | 3.14 | 2.22 | 0.97 | 2.16 |
| X=Me | Y | 2.30 | 1.40 | 3.16 | 2.79 | 2.25 | 0.88 | 1.99 |
| X=NH₃ | Y | 2.05 | 0.66 | 2.86 | 3.33 | 4.36 | 1.17 | 5.08 |
| Y=NM₃ | Not a clear HOMO-to-LUMO excitation |
| Y=NO₂ | 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=SiH₃ | LUMO is of a different character compared to that of the parent fulvene |
| X=CF₃ | Y=BF₂ | 2.20 | 1.33 | 3.27 | 2.83 | 2.47 | 0.87 | 2.13 |
| X=BF₂ | Y=BF₂ | 2.10 | 1.35 | 3.23 | 3.26 | 2.40 | 0.81 | 2.42 |
| X=BF₂ | Y=BF₂ | 2.26 | 1.33 | 3.29 | 1.95 | 2.48 | 0.59 | 1.47 |
| X=Cl | Y=Cl | 1.68 | 0.84 | 2.50 | 2.59 | 2.96 | 1.04 | 3.07 |
| X=CN | Y=CN | 1.90 | 1.22 | 2.94 | 2.66 | 2.41 | 0.91 | 2.18 |
| X=F | Y=F | 1.77 | 0.86 | 2.65 | 3.01 | 3.08 | 1.13 | 3.49 |
| X=Me | Y=Me | 1.81 | 0.94 | 2.63 | 2.75 | 2.79 | 1.05 | 2.92 |
| X=NH₃ | T₀ ground state |
| X=NM₃ | Y=NM₃ | 1.46 | 0.22 | 2.14 | 2.72 | 9.67 | 1.28 | 12.32 |
| X=NO₂ | Y=NO₂ | 2.18 | 1.38 | 3.25 | 2.44 | 2.35 | 0.75 | 1.76 |
| X=OH | Y=OH | 1.44 | 0.57 | 2.23 | 2.99 | 3.91 | 1.34 | 5.24 |
| X=OMe | Y=OMe | 1.48 | 0.66 | 2.23 | 3.00 | 3.39 | 1.35 | 4.56 |
| X=SH | Y=SH | 1.60 | 0.61 | 2.38 | 2.81 | 3.90 | 1.18 | 4.59 |
| X=SiH₃ | Y=SiH₃ | 2.16 | 1.40 | 3.10 | 2.82 | 2.21 | 0.91 | 2.01 |
| X=OMe | Y=BF₂ | LUMO primarily localized on the Y substituents |
| X=BF₂ | Y=BF₂ | HOMO and LUMO primarily localized on the Y substituents |
| X=CF₃ | Y=CF₃ | T₁ excitation is different to that of the parent fulvene |
| X=Cl | Y=Cl | 2.54 | 1.97 | 3.75 | 3.22 | 1.91 | 0.86 | 1.64 |
| X=Cl | Y=Cl | 2.45 | 1.71 | 3.44 | 3.41 | 2.01 | 0.99 | 1.99 |
| X=F | Y=F | 2.79 | 1.82 | 3.80 | 3.84 | 2.09 | 1.01 | 2.11 |
| X=Me | Y=Me | 2.57 | 1.79 | 3.60 | 3.42 | 2.01 | 0.95 | 1.91 |
| X=NH₃ | Y=NH₃ | 1.95 | 1.03 | 2.81 | 3.44 | 2.74 | 1.22 | 3.35 |
| X=NM₃ | Y=NM₃ | 2.32 | 1.34 | 3.18 | 3.37 | 2.37 | 1.06 | 2.52 |
| X=NO₂ | Y=NO₂ | T₁ excitation is different to that of the parent fulvene |
| X=OH | Y=OH | Not a clear HOMO-to-LUMO excitation |
| X=OMe | Y=OMe | Not a clear HOMO-to-LUMO excitation |
| X=SH | Y=SH | 2.13 | 1.45 | 3.00 | 3.46 | 2.07 | 1.15 | 2.39 |
| X=SiH₃ | Y=SiH₃ | 2.72 | 2.02 | 3.84 | 3.21 | 1.90 | 0.83 | 1.59 |
| X=SiH₃ | Y=BF₂ | 2.34 | 1.65 | 3.50 | 2.40 | 2.12 | 0.69 | 1.45 |

S10
|            | Y = BH₂ |  | REARRANGED |  |                         |  |
|------------|---------|---|------------|---|------------------------|---|
| Y = CF₃    | 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 = NH₂    | 1.69    | 0.52 | 2.44       | 3.11 | 4.67 | 1.27 | 5.94 |
| Y = NMe₂   | 1.88    | 0.98 | 2.58       | 3.39 | 2.62 | 1.31 | 3.45 |
| Y = NO₂    | 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 = SiH₃   | 2.32    | 1.51 | 3.28       | 2.67 | 2.17 | 0.81 | 1.77 |
Table S3. The $E(T_1)\nu$, $E(T_1)\alpha$, $E(S_1)$ and $E(T_2)$ of the differently substituted fulvenes sorted by $E(T_1)\alpha$. For label “REARRANGED” see Table S2.

| $X$   | $Y$   | $E(T_1)\nu$ | $E(T_1)\alpha$ | $E(S_1)$ | $E(T_2)$ | $E(T_2)/E(S_1)$ | $E(T_2)/E(T_1)$ |
|-------|-------|-------------|-----------------|----------|----------|-----------------|-----------------|
| NO₂   | NMē₂  | 1.65        | 0.10            | 2.33     | 2.92     | 23.80           | 1.25            | 29.83           |
| CN    | NMē₂  | 1.03        | 0.21            | 1.63     | 3.41     | 7.77            | 2.10            | 16.29           |
| CF₃   | NMē₂  | 1.46        | 0.22            | 2.14     | 2.72     | 9.67            | 1.28            | 13.32           |
| CN    | SH    | 0.98        | 0.38            | 1.62     | 2.70     | 4.24            | 1.67            | 7.08            |
| NO₂   | OH    | 1.43        | 0.44            | 2.17     | 2.86     | 4.94            | 1.31            | 6.49            |
| CN    | OH    | 1.19        | 0.45            | 1.89     | 2.84     | 4.20            | 1.50            | 6.30            |
| NO₂   | SH    | 1.50        | 0.45            | 2.19     | 2.82     | 4.84            | 1.29            | 6.23            |
| NO₂   | OMe   | 1.46        | 0.50            | 2.17     | 2.86     | 4.32            | 1.32            | 5.70            |
| SiH₃  | NH₂   | 1.69        | 0.52            | 2.44     | 3.11     | 4.67            | 1.27            | 5.94            |
| CN    | OMe   | 1.22        | 0.53            | 1.90     | 2.86     | 3.59            | 1.50            | 5.40            |
| CF₃   | OH    | 1.44        | 0.57            | 2.23     | 2.99     | 3.91            | 1.34            | 5.24            |
| CF₃   | SH    | 1.60        | 0.61            | 2.38     | 2.81     | 3.90            | 1.18            | 4.59            |
| Cl    | NH₂   | 1.62        | 0.64            | 2.42     | 3.29     | 3.81            | 1.36            | 5.17            |
| SH    | NH₂   | 2.05        | 0.66            | 2.86     | 3.33     | 4.36            | 1.17            | 5.08            |
| CF₃   | OMe   | 1.48        | 0.66            | 2.23     | 3.00     | 3.39            | 1.35            | 4.56            |
| NO₂   | BF₂   | 2.11        | 0.67            | 3.06     | 3.08     | 4.57            | 1.01            | 4.60            |
| CN    | F     | 1.54        | 0.72            | 2.32     | 2.72     | 3.21            | 1.17            | 3.77            |
| BF₂   | OH    | 1.89        | 0.72            | 2.78     | 3.81     | 3.84            | 1.37            | 5.26            |
| NO₂   | F     | 1.70        | 0.73            | 2.52     | 2.85     | 3.44            | 1.13            | 3.90            |
| CN    | Cl    | 1.49        | 0.78            | 2.23     | 2.61     | 2.87            | 1.17            | 3.36            |
| NO₂   | Cl    | 1.70        | 0.79            | 2.49     | 2.58     | 3.16            | 1.04            | 3.27            |
| BF₂   | OMe   | 1.93        | 0.83            | 2.79     | 3.89     | 3.37            | 1.39            | 4.71            |
| BF₂   | F     | 1.86        | 0.83            | 2.74     | 2.90     | 3.30            | 1.06            | 3.49            |
| CF₃   | Cl    | 1.68        | 0.84            | 2.50     | 2.59     | 2.96            | 1.04            | 3.07            |
| NO₂   | Me    | 1.78        | 0.85            | 2.54     | 2.67     | 2.98            | 1.05            | 3.15            |
| CF₃   | F     | 1.77        | 0.86            | 2.65     | 3.01     | 3.08            | 1.13            | 3.49            |
| H     | NH₂   | 1.74        | 0.87            | 2.59     | 3.70     | 2.98            | 1.43            | 4.27            |
| BH₂   | OMe   | 2.29        | 0.87            | 3.17     | 3.01     | 3.65            | 0.95            | 3.46            |
| BH₂   | F     | 2.39        | 0.88            | 3.39     | 2.82     | 3.87            | 0.83            | 3.23            |
| CN    | Me    | 1.63        | 0.90            | 2.36     | 2.69     | 2.61            | 1.14            | 2.97            |
| SiH₃  | OH    | 1.72        | 0.91            | 2.52     | 3.22     | 2.77            | 1.28            | 3.55            |
| BF₂   | Me    | 1.91        | 0.92            | 2.74     | 2.63     | 2.98            | 0.96            | 2.86            |
| BF₂   | SH    | 2.35        | 0.92            | 3.40     | 3.02     | 3.68            | 0.89            | 3.27            |
| F     | NH₂   | 2.00        | 0.93            | 2.94     | 3.31     | 3.17            | 1.12            | 3.57            |
| SiH₃  | SH    | 2.22        | 0.93            | 3.17     | 2.71     | 3.40            | 0.86            | 2.91            |
| CF₃   | Me    | 1.81        | 0.94            | 2.63     | 2.75     | 2.79            | 1.05            | 2.92            |
| Cl    | NMē₂  | 1.81        | 0.97            | 2.56     | 3.32     | 2.65            | 1.22            | 3.50            |
| SiH₃  | NMē₂  | 1.88        | 0.98            | 2.58     | 3.39     | 2.62            | 1.31            | 3.45            |
| Me    | NH₂   | 1.96        | 0.99            | 2.83     | 3.32     | 2.84            | 1.18            | 3.34            |
| SiH₃  | OMe   | 1.78        | 1.01            | 2.55     | 3.28     | 2.53            | 1.28            | 3.24            |
| X  | Y   | 1.67 | 1.02 | 2.47 | 3.13 | 2.42 | 1.27 | 3.06 |
|----|-----|------|------|------|------|------|------|------|
| Cl | SH  |      |      |      |      |      |      |      |
| Cl | OMe | 1.95 | 1.03 | 2.81 | 3.44 | 2.74 | 1.22 | 3.35 |
| Cl | SH  | 1.81 | 1.05 | 2.54 | 2.76 | 2.43 | 1.09 | 2.64 |
| H  | BH  | 1.88 | 1.06 | 2.64 | 2.60 | 2.49 | 0.99 | 2.45 |
| H  | NH2 | 1.98 | 1.06 | 2.87 | 3.50 | 2.70 | 1.22 | 3.30 |
| Cl | OH  | 1.85 | 1.06 | 2.70 | 3.32 | 2.54 | 1.23 | 3.12 |
| Cl | Cl  | 2.08 | 1.07 | 3.03 | 2.73 | 2.83 | 0.90 | 2.55 |
| H  | OH  | 1.97 | 1.08 | 2.89 | 3.74 | 2.67 | 1.29 | 3.45 |
| H  | NMe2| 1.93 | 1.09 | 2.76 | 3.65 | 2.52 | 1.32 | 3.34 |
| CN | CN  | 1.72 | 1.10 | 2.63 | 2.39 | 2.40 | 0.91 | 2.18 |
| SiH3| F   | 1.99 | 1.12 | 2.89 | 3.16 | 2.58 | 1.09 | 2.82 |
| H  | BF2 | 1.91 | 1.13 | 2.75 | 2.87 | 2.43 | 1.04 | 2.54 |
| H  | NO2 | 1.96 | 1.13 | 2.80 | 2.90 | 2.47 | 1.03 | 2.56 |
| BF2| BH2 | 2.03 | 1.13 | 3.23 | 3.39 | 2.85 | 1.05 | 2.99 |
| H  | CN  | 1.91 | 1.14 | 2.74 | 2.52 | 2.41 | 0.92 | 2.21 |
| NO2| CN  | 1.86 | 1.16 | 2.84 | 2.61 | 2.46 | 0.92 | 2.26 |
| SiH3| Cl  | 1.95 | 1.16 | 2.82 | 2.72 | 2.43 | 0.97 | 2.34 |
| NO2| SiH3| 2.00 | 1.18 | 2.81 | 2.76 | 2.39 | 0.98 | 2.34 |
| Me | NMe2| 2.13 | 1.18 | 2.97 | 3.06 | 2.51 | 1.03 | 2.59 |
| Cl | OMe| 1.93 | 1.19 | 2.76 | 3.30 | 2.32 | 1.20 | 2.78 |
| SiH3| Me | 2.02 | 1.20 | 2.87 | 2.77 | 2.39 | 0.97 | 2.31 |
| BF2| SiH3| 2.04 | 1.21 | 2.91 | 2.52 | 2.41 | 0.87 | 2.09 |
| CF3| CN  | 1.90 | 1.22 | 2.94 | 2.66 | 2.41 | 0.91 | 2.18 |
| H  | SH  | 2.06 | 1.22 | 2.98 | 3.46 | 2.44 | 1.16 | 2.83 |
| NMe2| NH2| 2.37 | 1.23 | 3.04 | 3.94 | 2.46 | 1.30 | 3.20 |
| CN | SiH3| 1.93 | 1.23 | 2.73 | 2.54 | 2.22 | 0.93 | 2.06 |
| F  | NMe2| 2.18 | 1.23 | 3.07 | 3.39 | 2.49 | 1.10 | 2.74 |
| CN | BH2 | 1.94 | 1.24 | 2.98 | 3.04 | 2.40 | 1.02 | 2.45 |
| CN | NO2 | 1.99 | 1.25 | 2.91 | 2.41 | 2.32 | 0.83 | 1.93 |
| Cl | F   | 2.13 | 1.27 | 3.07 | 3.22 | 2.41 | 1.05 | 2.53 |
| BH2| Cl  | 2.43 | 1.28 | 3.42 | 2.93 | 2.67 | 0.86 | 2.29 |
| Me | OH  | 2.14 | 1.29 | 3.07 | 3.48 | 2.39 | 1.13 | 2.70 |
| NO2| NO2 | 2.10 | 1.29 | 3.09 | 2.34 | 2.40 | 0.76 | 1.82 |
| Me | SH  | 1.99 | 1.29 | 2.86 | 3.09 | 2.21 | 1.08 | 2.39 |
| SH | OH  | 2.09 | 1.29 | 2.92 | 3.15 | 2.25 | 1.08 | 2.43 |
| BF2| CN  | 2.15 | 1.30 | 3.32 | 2.53 | 2.56 | 0.76 | 1.95 |
| NO2| CF3 | 2.24 | 1.30 | 3.22 | 2.43 | 2.48 | 0.76 | 1.87 |
| Cl | Cl  | 2.06 | 1.31 | 2.97 | 2.92 | 2.27 | 0.98 | 2.23 |
| CN | BF2 | 2.06 | 1.31 | 3.01 | 2.45 | 2.29 | 0.81 | 1.86 |
| H  | OMe| 2.05 | 1.32 | 2.94 | 3.56 | 2.23 | 1.21 | 2.70 |
| CF3| BF2 | 2.20 | 1.33 | 3.27 | 2.83 | 2.47 | 0.87 | 2.13 |
| CF3| CF3 | 2.26 | 1.33 | 3.29 | 1.95 | 2.48 | 0.59 | 1.47 |
| OMe| NMe2| 2.32 | 1.34 | 3.18 | 3.37 | 2.37 | 1.06 | 2.52 |
| H  | CF3 | 2.16 | 1.34 | 3.13 | 3.10 | 2.33 | 0.99 | 2.31 |
| CF3| BH2 | 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 = CF₃ | 2.13 | 1.36 | 3.03 | 2.44 | 2.23 | 0.81 | 1.80 |
| X = CF₃| Y = NO₂ | 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 = BF₂| Y = BF₂ | 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 = CF₃| Y = SiH₃ | 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 = BF₂| Y = CF₃ | 2.46 | 1.45 | 3.57 | 3.66 | 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 = SiH₃| 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 = SiH₃ | 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 = SiH₃| Y = SiH₃ | 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 = BH₂| 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 = BH₂ | 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 = SiH₃| Y = CF₃ | 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 = SiH₃| Y = BF₂ | 2.34 | 1.65 | 3.50 | 2.40 | 2.12 | 0.69 | 1.45 |
| X = Cl | Y = NO₂ | 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 = NO₂ | 2.09 | 1.68 | 3.32 | 2.92 | 1.98 | 0.88 | 1.74 |
| X = NMe₂| Y = NMe₂ | 2.56 | 1.69 | 3.20 | 3.38 | 1.90 | 1.05 | 2.00 |
| X = H | Y = NO₂ | 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 | Y = 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 = SiH₃ | 2.45 | 1.72 | 3.47 | 2.93 | 2.02 | 0.84 | 1.70 |
| X = Cl | Y = BF₂ | 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 | 3.50 | 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$_2$ | 2.45 | 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 = NH$_2$ | Y = Me  | 2.78 | 1.97 | 3.58 | 3.16 | 1.81 | 0.88 | 1.60 |
| Y = H    | Y = OMe | 3.02 | 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 = NH$_2$ | 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 = NH$_2$ | 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 |
| X = H | Y = H | S_0 | T_{1v} | T_{1a} | S_1 | T_2 |
|-------|-------|-----|--------|--------|-----|-----|
|       |       | -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 | -731.12909 |
| 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 | REARRANGED | REARRANGED | REARRANGED | REARRANGED |
| Y = NMe_2 |    | REARRANGED | REARRANGED | REARRANGED | REARRANGED | REARRANGED |
| Y = NO_2 |    | REARRANGED | REARRANGED | REARRANGED | REARRANGED | REARRANGED |
| Y = OH |       | -830.83764 | -830.76816 | -830.81104 | -830.73551 | -830.69773 |
| Y = OMe |       | -909.43153 | -909.36052 | -909.40116 | -909.32903 | -909.38457 |
| 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 |
|-------|-------|--------------------------------------------------|
|       |       | 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 |       | -481.35239 | -481.34605 | -481.49171 | -481.39948 | |
| Y = Me |       | REARRANGED | Degenerate states |
| 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 | -909.38457 |
| X = Cl |       | -1599.58440 | -1599.49688 | -1599.52100 | -1599.45356 | -1599.48212 |
| Y = BF_2 |       | -1202.23997 | -1202.15864 | -1202.18144 | -1202.11234 | -1202.13807 |
| Y = BH_2 |       | -1825.55035 | -1825.45521 | -1825.48309 | -1825.41445 | -1825.44767 |
| Y = CF_3 |       | -2070.56753 | -2070.49192 | -2070.51940 | -2070.45840 | -2070.46024 |
| Y = Cl |       | -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 | -1261.96552 |
| 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 |       | -1380.41824 | -1380.34721 | -1380.37457 | -1380.31674 | -1380.29683 |
| Y = OMe |      | -1947.74538 | -1947.68405 | -1947.70785 | -1947.65470 | -1947.63040 |
| Y = SiH₂ | -1732.73598 | -1732.64585 | -1732.67265 | -1732.60832 | -1732.62831 |
| Y = BF₂ | -864.86234 | -864.78650 | -864.81405 | -864.75159 | -864.77236 |
| Y = BH₂ | -467.52201 | -467.45081 | -467.47648 | -467.41265 | -467.41034 |
| Y = CF₃ | -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 | -601.05031 |
| 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 = NMe₂ | -684.57038 | -684.53259 | -684.56268 | -684.51055 | |
| Y = NH₂ | T<sub>0</sub> ground state |
| Y = NO₂ | -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 | -1212.91320 | -1212.96679 | -1212.92704 |
| Y = SiH₃ | -998.01801 | -997.94696 | -997.97269 | -997.91756 | -997.92463 |
| X = F | Y = BF₂ | -878.90114 | -878.85053 | -878.82649 | -878.75325 | -878.78762 |
| Y = BH₂ | -481.48555 | -481.47281 | -481.46815 | |
| Y = CF₃ | -1104.86773 | -1104.76181 | -1104.78970 | -1104.71407 | -1104.74438 |
| Y = Cl | -1349.88269 | -1349.79342 | -1349.82160 | -1349.75586 | -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 = NH₂ | -541.39654 | -541.32306 | -541.36246 | -541.28850 | -541.27501 |
| Y = NMe₂ | -698.59242 | -698.51214 | -698.54703 | -698.47959 | -698.46799 |
| Y = NO₂ | Not a clear HOMO-to-LUMO excitation |
| Y = OH | -581.13773 | -581.05392 | -581.08681 | -581.01688 | -581.01490 |
| Y = OMe | -659.72987 | -659.63415 | -659.67475 | -659.60716 | -659.60805 |
| Y = SH | -1227.05818 | -1226.98155 | -1227.00846 | -1226.94703 | -1226.94209 |
| Y = SiH₃ | -1012.04590 | -1011.94548 | -1011.97193 | -1011.90124 | -1011.93091 |
| X = H | Y = BF₂ | -680.39326 | -680.30386 | -680.32617 | -680.25493 | -680.28852 |
| Y = BH₂ | LUMO primarily localized on the Y substituents |
| Y = CF₃ | -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 | |
| Y = NH₂ | -342.88483 | -342.82102 | -342.85299 | -342.78979 | -342.74887 |
| Y = NMe₂ | -500.07957 | -500.00860 | -500.03937 | -499.97831 | -499.94547 |
| Y = NO₂ | -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 = SiH₃ | -813.53102 | -813.43893 | -813.46562 | -813.39813 | -813.41579 |
| X = Me | Y = BF₂ | T<sub>1</sub> excitation is different to that of the parent fulvene |
| X = NH₂ | Y = BF₂ | REARRANGED |
|---|---|---|
| Y = BH₂ | | REARRANGED |
| Y = CF₃ | | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = Cl | -1262.12506 | -1262.01607 | -1261.98048 | -1261.98881 |
| Y = CN | -541.41743 | -541.30693 | -541.33670 | -541.27022 | -541.27555 |
| Y = F | -421.52981 | -421.42265 | -421.44698 | -421.38583 | -421.39771 |
| Y = Me | -578.69759 | -578.61918 | -578.65408 | -578.58826 | -578.58508 |
| Y = NO₂ | | Not a clear HOMO-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 = SiH₃ | -1107.16687 | -1107.09370 | -1107.11938 | -1107.06188 | -1107.05331 |

| X = NMe₂ | Y = BF₂ | REARRANGED |
|---|---|---|
| Y = BH₂ | | REARRANGED |
| Y = CF₃ | | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = Cl | -1419.31419 | -1419.20666 | -1419.23321 | -1419.17903 | -1419.18704 |
| Y = CN | -698.60304 | -698.49494 | -698.52455 | -698.46356 | -698.47096 |
| Y = F | -578.71613 | -578.61403 | -578.64368 | -578.58469 | -578.59987 |
| Y = Me | -610.80961 | -610.72258 | -610.76435 | -610.69805 | -610.66489 |
| Y = NMe₂ | -768.00926 | -767.91536 | -767.94729 | -767.95414 |
| Y = NO₂ | | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = OH | | T₁ excitation is different to that of the parent fulvene |
| Y = OMe | | T₁ excitation is different to that of the parent fulvene |
| Y = SH | | Both T₁ and S₁ excitations are different to that of the parent fulvene |
| Y = SiH₃ | | Both T₁ and S₁ excitations are different to that of the parent fulvene |

| X = NO₂ | Y = BF₂ | | REARRANGED |
|---|---|---|
| Y = BH₂ | | REARRANGED |
| Y = CF₃ | -1315.33487 | -1315.25244 | -1315.28710 | -1315.21654 | -1315.24540 |

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Both T₁ and S₁ excitations are different to that of the parent fulvene.
| X   | Y   | T1 Excitations | S1 Excitations | T2 Excitations | S2 Excitations |
|-----|-----|----------------|----------------|----------------|----------------|
| OH  | Cl  | -1560.35805    | -1560.29554    | -1560.32911    | -1560.26655    | -1560.26331    |
|     | CN  | -825.64763     | -825.57923     | -825.60515     | -825.54310     | -825.55155     |
|     | F   | -839.65194     | -839.58934     | -839.62503     | -839.55937     | -839.54709     |
|     | Me  | -719.78958     | -719.72417     | -719.75834     | -719.69636     | -719.69132     |
|     | NH2 | Not a clear HOMO-to-LUMO excitation |
|     | NMe2| -909.07684     | -909.01616     | -909.07324     | -908.99111     | -908.96940     |
|     | NO2 | -1050.16616    | -1050.08901    | -1050.11879    | -1050.05265    | -1050.08007    |
|     | OH  | -791.61972     | -791.56703     | -791.60355     | -791.53991     | -791.51479     |
|     | OMe | -870.21378     | -870.16012     | -870.19535     | -870.13419     | -870.10868     |
|     | SH  | -1437.53764    | -1437.48248    | -1437.52098    | -1437.45701    | -1437.43392    |
|     | BF3 | -1222.52954    | -1222.45595    | -1222.48633    | -1222.42615    | -1222.42827    |
|     | H   | Both T1 and S1 excitations are different to that of the parent fulvene |
|     | BH2 | Both T1 and S1 excitations are different to that of the parent fulvene |
|     | CF3 | T1 excitation is different to that of the parent fulvene |
|     | Cl  | -1301.84726    | -1301.75558    | -1301.78272    | -1301.71789    | -1301.71861    |
|     | CN  | LUMO primarily localized on the Y substituents |
|     | F   | -581.13922     | -581.04478     | -581.07595     | -581.00584     | -581.00448     |
|     | Me  | -461.26637     | -461.16957     | -461.19848     | -461.13070     | -461.13820     |
|     | NH2 | -493.35983     | -493.28708     | -493.32082     | -493.25443     | -493.23118     |
|     | NMe2| HOMO is of a different character compared to that of the parent fulvene |
|     | NO2 | REARRANGED |
|     | OH  | -533.11923     | -533.02052     | -533.04791     | -532.98378     | -532.97752     |
|     | OMe | -611.68979     | -611.60113     | -611.63540     | -611.56695     | -611.57049     |
|     | SH  | -1179.02369    | -1178.94417    | -1178.96942    | -1178.91106    | -1178.89395    |
|     | SiH3| LUMO primarily localized on the Y substituents |
|     | BF3 | -680.37725     | -680.30703     | -680.33567     | -680.27608     | -680.27184     |
|     | BH2 | -283.02474     | -282.95564     | -282.98574     | -282.92779     | -282.92922     |
|     | CF3 | -906.34182     | -906.26261     | -906.29250     | -906.22680     | -906.22808     |
|     | Cl  | -1151.37446    | -1151.28553    | -1151.31568    | -1151.24810    | -1151.26662    |
|     | CN  | -416.65755     | -416.58752     | -416.61568     | -416.55682     | -416.56493     |
|     | F   | -430.68265     | -430.58013     | -430.51154     | -430.53584     | -430.57065     |
|     | Me  | -310.79405     | -310.69687     | -310.72617     | -310.65615     | -310.67989     |
|     | NH2 | Both T1 and S1 excitations are different to that of the parent fulvene |
|     | NMe2| T1 excitation is different to that of the parent fulvene |
|     | NO2 | -641.17081     | -641.09862     | -641.12914     | -641.06776     | -641.06431     |
|     | OH  | -382.64517     | -382.54219     | -382.57160     | -382.50037     | -382.52277     |
|     | OMe | -461.23032     | -461.11891     | -461.15732     | -461.07799     | -461.10939     |
|     | SH  | -1028.55370    | -1028.49405    | -1028.49364    | -1028.42856    | -1028.44891    |
|     | SiH3| -813.52405     | -813.43957     | -813.47039     | -813.40391     | -813.41739     |
|     | BF3 | Both T1 and S1 excitations are different to that of the parent fulvene |
|     | BH2 | Both T1 and S1 excitations are different to that of the parent fulvene |
|     | CF3 | T1 excitation is different to that of the parent fulvene |
|     | Cl  | -1947.75175    | -1947.67019    | -1947.69975    | -1947.63899    | -1947.65157    |
|     | CN  | T1 excitation is different to that of the parent fulvene |
| X = CF₂ | Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
|--------|--------|------------------------------------------------------|
| Y = BH₂ | Not a clear HOMO-to-LUMO excitation | |
| Y = CF₃ | Not a clear HOMO-to-LUMO excitation | |
| Y = Cl | Not a clear HOMO-to-LUMO excitation | |
| Y = F | Not a clear HOMO-to-LUMO excitation | |
| Y = Me | Not a clear HOMO-to-LUMO excitation | |
| X = OMe | Y = BF₂ | T₁ excitation is different to that of the parent fulvene |
| Y = BH₂ | Not a clear HOMO-to-LUMO excitation | |
| Y = CF₃ | Not a clear HOMO-to-LUMO excitation | |
| Y = Cl | Not a clear HOMO-to-LUMO excitation | |
| Y = F | Not a clear HOMO-to-LUMO excitation | |
| Y = Me | Not a clear HOMO-to-LUMO excitation | |
| Y = NH₂ | -924.23791 | -924.17569 | -924.21870 | -924.14820 | -924.12374 |
| Y = NMe₂ | -1081.43770 | -1081.36877 | -1081.40155 | -1081.34281 | -1081.31300 |
| Y = NH₂ | 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 = SiH₃ | -1394.87748 | -1394.79215 | -1394.82202 | -1394.75711 | -1394.77940 |
Table S5. NICS(1)zz values in the S\(_0\) and T\(_1\) states of the differently substituted fulvenes. For label “REARRANGED” see Table S2.

| X=H  | Y=H  | S\(_0\) | T\(_1\) | HOMA |
|------|------|--------|--------|------|
| 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 | -0.55 | 0.55 |
| Y=SH  | -0.6  | -11.4 | -0.37 | 0.43 |
| Y=SiH\(_3\) | 5.4   | -3.2  | -0.83 | 0.17 |

X=BF\(_2\)  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\(_2\)  T\(_1\) excitation is different to that of the parent fulvene

| 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  | 5.6   | -4.6  | -0.48 | 0.51 |
| X = CN | Y = OMe | 5.0 | -4.2 | -0.49 | 0.46 |
|-------|---------|-----|------|-------|------|
| Y = SH | -0.8 | -3.4 | -0.46 | 0.35 |
| Y = SiH₃ | -5.7 | 9.3 | -0.31 | -0.04 |
| X = F  | Y = BF₂ | 2.5 | 1.7 | -0.33 | 0.17 |
| Y = BH₂ | 0.9 | -6.1 | -0.36 | 0.39 |
| Y = CF₂ | 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   | -5.7 | 5.0 | -0.61 | 0.50 |
| Y = Me  | 13.0 | -4.8 | -0.75 | 0.41 |
| Y = NH₂ | T₀ ground state |
| Y = NMe₂ | 21.5 | -10.5 | -0.66 | 0.46 |
| Y = NO₂ | 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 = SiH₃ | 4.5 | 0.4 | -0.59 | 0.20 |
| X = F  | Y = BF₂ | -14.0 | 15.5 | 0.18 | -0.31 |
| Y = BH₂ | -13.5 | 16.2 | 0.19 | -0.50 |
| Y = CF₂ | -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 | 0.50 |
| Y = Me  | -4.9 | 4.1 | -0.24 | 0.35 |
| Y = NH₂ | 0.9 | -9.9 | -0.35 | 0.63 |
| Y = NMe₂ | 0.1 | -7.8 | -0.34 | 0.57 |
| Y = NO₂ | 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 = SiH₃ | -10.7 | 10.6 | -0.04 | 0.03 |
| X = H  | Y = BF₂ | -10.5 | 14.4 | -0.07 | -0.20 |
| Y = BH₂ | LUMO primarily localized on the Y substituents |
| Y = CF₂ | -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 = NH₂ | 10.4 | -11.3 | -0.59 | 0.54 |
| Y = NMe₂ | 8.0 | -9.3 | -0.57 | 0.38 |
| Y = NO₂ | -5.6 | 14.4 | -0.05 | 0.07 |
| Y = OH  | 6.2 | -8.9 | -0.47 | 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 | T1 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 = NH2 | -4.8 | -10.8 | -0.23 | 0.50 |
| Y = NMe2 | Not a clear HOMO-to-LUMO excitation |
| Y = NO2 | -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 = SiH3 | LUMO is of a different character compared to that of the parent fulvene |

| X=CF3 | Y = BF3 | 2.3 | -0.7 | -0.68 | 0.13 |
|-------|---------|-----|------|--------|-----|
| Y = BH2 | 1.6 | -6.7 | -0.63 | 0.18 |
| Y = CF3 | 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 = NH2 | 14.6 | -9.7 | -0.89 | 0.45 |
| Y = NMe2 | 14.9 | -9.7 | -0.89 | 0.45 |
| Y = NO2 | 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 = SiH3 | 5.1 | -1.6 | -0.99 | 0.09 |

| X=OMe | Y = BF3 | -5.3 | 15.1 | -0.36 | 0.12 |
|-------|---------|------|-----|--------|-----|
| Y = BH2 | REARRANGED |
| Y = CF3 | -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 |
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) levels.

| Fulvene | $E(T_1)_{a}$ | $E(S_1)c$ | $E(T_2)d$ | $E(S_1)/E(T_1)_{a}$ | $E(T_2)/E(S_1)$ | $E(T_2)/E(T_1)_{a}$ |
|---------|--------------|------------|------------|----------------------|------------------|---------------------|
| X = CN, Y = NMe₂ | 0.21, 0.56 | 1.63, 2.04 | 3.41, 3.28 | 7.76, 3.64 | 2.09, 1.61 | 16.24, 5.86 |
| X = NO₂, Y = NH₂ | 0.28, 0.21 | 1.68, 1.52 | 3.21, 3.32 | 6.00, 7.24 | 1.91, 2.18 | 11.46, 15.78 |
| X = CF₃, Y = NMe₂ | 0.46, 0.66 | 2.18, 2.55 | 2.89, 3.17 | 4.74, 3.86 | 1.33, 1.24 | 6.28, 4.79 |
| X = CN, Y = OMe | 0.53, 0.61 | 1.90, 2.26 | 2.86, 3.13 | 3.58, 3.70 | 1.51, 1.38 | 5.40, 5.11 |
| X = CN, Y = F | 0.72, 0.93 | 2.32, 2.66 | 2.72, 3.07 | 3.22, 2.86 | 1.17, 1.15 | 3.78, 3.29 |
| X = BF₂, Y = F | 0.83, 0.77 | 2.74, 3.04 | 2.90, 2.96 | 3.30, 3.95 | 1.06, 0.97 | 3.49, 3.83 |
| X = OMe, Y = NH₂ | 1.03, 1.26 | 2.81, 3.10 | 3.44, 3.62 | 2.73, 2.46 | 1.22, 1.17 | 3.34, 2.88 |
| X = CN, Y = SiH₃ | 1.23, 1.25 | 2.73, 3.04 | 2.54, 2.75 | 2.22, 2.43 | 0.93, 0.90 | 2.07, 2.19 |

*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 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 $E(S_1)$, $E(T_1)_a$ 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.

|   | $E(S_1)_{exp}$ | $E(S_1)_a$ | $E(T_1)_{exp}$ | $E(T_1)_a$ | $E(S_1)/E(T_1)_a$ | $E(S_1)/E(T_1)$ | $E(S_1)_a/E(T_1)_a$ |
|---|---------------|-------------|----------------|------------|-------------------|---------------|---------------------|
| 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 |
| TBuEDCF | - | 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 T₁ excitons formed in an efficient singlet fission chromophore should be long-lived, we investigated the probability for spin-forbidden T₁/S₀ state processes such as intersystem crossing and phosphorescence in fulvenes. If a triplet exciton is close to a T₁/S₀ crossing point with high spin-orbit coupling (SOC), leading to rapid decay to the S₀ state, the efficiency will be hampered. However, the SOC elements for T₁/S₀ in our eight fulvenes computed at TD-M06-2X level range from 0.4 to 2.8 cm⁻¹ (Table S7) which is typical of weak couplings and indicating that intersystem crossing will not impede the singlet fission process.

Table S9. Spin-orbit coupling (∂T₁[H]|S₀>) elements (in cm⁻¹) and %TAE([T]) values computed at CCSD(T)/aug-cc-pVDZ level for a small selection of fulvenes.

| System | <T₁|H|S₀> | %TAE([T]) |
|--------|-------|----------|
| X = CN  | 1.0   | 3.145     |
| Y = NMe₂ |      |          |
| X = NO₂ | 1.1   | 3.216     |
| Y = NH₂ |      |          |
| X = CF₃  | 1.8   | 2.516ᵃ    |
| Y = NMe₂ |      |          |
| X = CN  | 0.3   | 2.831     |
| Y = OMe |      |          |
| X = NO₂ | 1.3   | 2.738     |
| Y = BF₂ |      |          |
| X = CN  | 0.4   | 3.766     |
| Y = F   |      |          |
| X = BF₂ | 1.7   | 2.613     |
| Y = F   |      |          |
| X = OMe | 1.7   | 2.964     |
| Y = NH₂ |      |          |
| X = CN  | 0.4   | 4.105     |
| Y = SiH₃|      |          |
| X = CN  | 2.8   | 3.629     |
| Y = BF₂ |      |          |
| X = BF₂ | 0.5   | 3.235ᵃ    |
| Y = CF₃ |      |          |
| X = BF₂ | 0.4   | 1.968     |
| Y = NO₂ |      |          |
| X = NH₂ | 1.9   | 2.624ᵃ    |
| Y = NMe₂ |      |          |

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 $\%\text{TAE}_e(T)$, i.e., the percentage of the perturbative triples correction (T) to the total CCSD(T) atomization energy, proposed by Karton et al. $^5$ The computed $\%\text{TAE}_e(T)$ values for the $S_0$ states of the fulvenes in Figure 5 are found in the range 2.0 - 4.1 % (Table S7), 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 $X = \text{CN}$ and $Y = \text{NH}_2$, and (B) the fulvene with $X = \text{NH}_2$ and $Y = \text{CN}$. 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 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, \( \eta \), of UHF natural orbitals as,

\[ T_n = \frac{\eta_{HOMO-n} - \eta_{LUMO}}{2} \]

Diradical (\( n=0 \)) and tetraradical (\( n=1 \)) characters have been calculated (Table Y).

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 $E(T_1)$, $E(S_1)$, and $E(T_2)$ vary as functions of the CC bond lengths marked in red of four fulvenes, (A) $X = CN$, $Y = H$, (B) $X = NH_2$, $Y = H$, (C) $X = F$, $Y = BF_2$, and (D) $X = F$, $Y = NH_2$. 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.

| $X$     | C2-C3 bond | C1-C2/C3-C4 |
|---------|------------|-------------|
| H       | 1.00 – 1.13| 1.04 – 1.16 |
| CN      | 0.83 – 0.86| 0.84 – 0.96 |
| NH$_2$  | 1.04 – 1.48*| 1.04 – 1.17 |
| F, BF$_2$ | 1.40 – 1.49| 1.41 – 1.51 |
| F, 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 $E(T_1)_{a}$ plotted vs. $\Delta$NICS(1)$_{zz,T1v-S0}$, and (F) $\Delta E(S_1-T_1)_{av}$ plotted vs. $\Delta$NICS(1)$_{zz,T1v-S0}$ calculated at GIAO/(U)M06-2X/6-311+G(d,p) level.
Figure S4: The $E(T_{1a})$ plotted vs. (A) NICS(1)$_{T1}$ and (B) HOMA$_{T1}$, (C) HOMA$_{T1}$ vs. NICS(1)$_{T1}$ and (D) $\Delta$HOMA$_{T1-S0}$ vs. $\Delta$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 for 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.

![Diagram](image)

$R = \text{i}^\text{Bu} \, (\text{SCBD}_1)$
$R = \text{SiMe}_3 \, (\text{SCBD}_2)$

$95\% \quad 98\%$

$R = \text{H}_2\text{C}-\text{CH}_2 \, (\text{SCBD}_3)$
$R = \text{CH}_2 \, (\text{SCBD}_4)$

$98\% \quad 98\%$

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

| Table S13. The $\Delta E(S_{1}-T_{1})_{va}$ of CBD and substituted CBDs (SCBD). |
|-----------------------------|
| **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 $\Delta$NICS(1)$_{zz,T1-S0}$ 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.

![Diagram of substituted pentalenes]

**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).

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

**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 $s$- and $as$-indacenes. In all the cases the major configuration in the $S_1$ state is the HOMO to LUMO transition.

![Diagram of substituted indacenes]

|       | $s$-IND | $s$-SIND1 | $s$-SIND2 |
|-------|---------|-----------|-----------|
| $R$ = H | 100%    | 100%      | 98%       |
| $R$ = Me|          |           |           |
| $R$ = Ph|          |           |           |

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

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.

|        | $\Delta E(S_1-T_1)_{va}$ |
|--------|---------------------------|
| $s$-IND | 0.95                      |
| $s$-SIND1 | 1.06                     |
| $s$-SIND2 | 0.87                      |
| $as$-IND | 1.41                      |
| $as$-SIND1 | 1.39                     |
| $as$-SIND2 | 1.38                      |
| $as$-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.

![Diagram of benzannelated CBDs]

**Figure S13.** Percentage 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.

| BENZCBD  | Excited State | Singlet  | Energy (eV) | Wavelength (nm) | $f$ | $<S^2>$ |
|----------|---------------|----------|-------------|----------------|-----|---------|
| BENZCBD1 | Singlet-B2    | 3.1464   | 394.05      | 0.000          | 0.70546 | 0.000 |
| BENZCBD2 | Singlet-A'    | 2.5678   | 482.84      | 0.000          | 0.68931 | 0.0056 |
| BENZCBD3 | Singlet-B2    | 3.4082   | 363.78      | 0.000          | 0.69960 | 0.0021 |
| BENZCBD4 | Singlet-B2    | 3.5941   | 344.96      | 0.000          | 0.70153 | 0.0000 |
| BENZCBD5 | Singlet-B2    | 2.3528   | 526.96      | 0.000          | -0.10722 | 0.0293 |
Table S19. Oscillator strengths for the \( S_1 \) transition of benzannelated CBDs (BENZCBD).

| 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:

|      |          | 53 -> 54 | 53 -> 58 | \( \langle S^2 \rangle \) | Excited State | E \( (eV) \) | \( \lambda \) nm | f      |
|------|----------|----------|----------|-----------------|--------------|----------|-------------|------|
| BENZCBD6 | 3.0363   | 0.68787  | 0.12273  | 0.68582         | Singlet-A'   | 3.0363 eV | 408.35 nm  | 0.0121 |
| BENZCBD7 | 3.9019   | 0.58997  | 0.12273  | 0.68582         | Singlet-A1   | 3.9019 eV | 317.76 nm  | 0.1300 |
| BENZCBD8 | 2.8436   | 0.68748  | 0.11588  | 0.68748         | Singlet-B2   | 2.8436 eV | 436.01 nm  | 0.0416 |
| BENZCBD9 | 2.5661   | 0.69558  |          | 0.69558         | Singlet-AG   | 2.5661 eV | 483.16 nm  | 0.0000 |
| BENZCBD10| 2.3637   | 0.69583  |          | 0.69583         | Singlet-A'   | 2.3637 eV | 524.54 nm  | 0.0106 |
| BENZCBD11| 2.1581   | 0.69816  |          | 0.69816         | Singlet-B3G  | 2.1581 eV | 574.50 nm  | 0.0000 |
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 $\sim$0.2 eV below the ideal $E(T_1)$ value. To examine if $E(T_1)$ can be increased this tunability we regarded the C$_8$-C$_9$ 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 S7). 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 $E(T_1)$, $E(S_1)$ and $E(T_2)$ energies of bent BENZCBD2 as a function of the $r_{C8-C9}$ 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 $E(T_1)$, $E(S_1)$ and $E(T_2)$ as a function of benzannelation in selected benzannelated 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 for pentalene and a few BENZCBD in the $T_1$ 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[1]phenanthrene

**BENZCBD6**  
benzo[a]biphenylene

**BENZCBD7**  
benzo[b]biphenylene

**BENZCBD8**  
benzo[3,4]cyclobuta-[1,2-]phenanthrene

**BENZCBD9**  
dibenzo[a,g]biphenylene

**BENZCBD10**  
naphtho[1',2':3,4]cyclobuta-[1,2-]phenanthrene

**BENZCBD11**  
cyclobuta[1,2-;3,4-]-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'                     |
| <S**2>=0.000                                   |
| 40 -> 41                                       |
| 0.70549                                        |
| **BENZPENT2**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 52 -> 54                                       |
| 0.18111                                        |
| 53 -> 54                                       |
| 0.67621                                        |
| **BENZPENT3**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 51 -> 54                                       |
| -0.10499                                       |
| 52 -> 54                                       |
| 0.10685                                        |
| 53 -> 54                                       |
| 0.68813                                        |
| **BENZPENT4**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 51 -> 54                                       |
| 0.13553                                        |
| 53 -> 54                                       |
| 0.69017                                        |
| **BENZPENT5**                                   |
| Excited State 1: Singlet-AG                     |
| <S**2>=0.000                                   |
| 53 -> 54                                       |
| 0.70286                                        |
| **BENZPENT6**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 63 -> 67                                       |
| -0.10523                                       |
| 66 -> 67                                       |
| 0.68837                                        |
| **BENZPENT7**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 66 -> 67                                       |
| 0.68727                                        |
| **BENZPENT8**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 64 -> 67                                       |
| -0.10364                                       |
| 66 -> 67                                       |
| 0.69199                                        |
| **BENZPENT9**                                   |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 65 -> 67                                       |
| 0.56288                                        |
| 66 -> 67                                       |
| -0.41235                                       |
| **BENZPENT10**                                  |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 65 -> 67                                       |
| 0.56288                                        |
| 66 -> 67                                       |
| -0.41235                                       |
| **BENZPENT11**                                  |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 66 -> 67                                       |
| 0.69908                                        |
| **BENZPENT12**                                  |
| Excited State 1: Singlet-A'                     |
| <S**2>=0.000                                   |
| 79 -> 80                                       |
| 0.69072                                        |
| **BENZPENT13**                                  |
| Excited State 1: Singlet-A'                     |
| <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 |
| 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 S\(^1\) 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 |
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)BENZPENT15 has shown to provide an entry point to singlet fission as the excitation occurs in the S2 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 S1 excitation is from HOMO to LUMO, yet for bis(styryl)BENZPENT5, the excitation if from HOMO-1 to LUMO. Yet, as the S1 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 $E(T_1)$, $E(S_1)$ and $E(T_2)$ as functions of benzannelation 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 $S_0$ and $T_1$ states calculated at GIAO/M06-2X/6-311+G(d,p) level. BENZPENT17 is unsymmetric in the $S_0$ 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 benzannelated 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.

|                  | $E(T_1)_v$ | $E(T_1)_a$ | $E(S_1)_v$ | $E(S_1)_a$ | $E(S_1)_v/E(T_1)_v$ | $E(S_1)_a/E(T_1)_a$ | $E(S_1)_v/E(S_1)_a$ | $E(T_1)_v - E(T_1)_a$ |
|------------------|-----------|-----------|-----------|-----------|---------------------|---------------------|---------------------|---------------------|
| 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                |
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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.

|     | $\Delta E(S_1-T_1)_{va}$ |
|-----|--------------------------|
| NO$_2$ | 0.92                     |
| CN   | 1.83                     |
| H    | 1.86                     |
| Me   | 2.01                     |
| OH   | 2.09                     |
| NH$_2$ | 2.97                   |

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.

|     | $\Delta E(S_1-T_1)_{va}$ |
|-----|--------------------------|
| CN  | 1.47                     |
| H   | 1.54                     |
| Cl  | 2.08                     |
| F   | 1.79                     |
| NH$_2$ | 1.83                 |
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.

| $X, Y$          | $\Delta E(S_1-T_{1,\alpha})$ | $\Delta E(S_1-T_{1,\nu})$ |
|-----------------|-------------------------------|----------------------------|
| $X = H$         | 2.34                          | 1.65                       |
| $X, Y = F$      | 2.29                          | 1.60                       |
| $X = F$ $Y = Me$| 2.27                          | 1.58                       |
| $X = F$ $Y = SiH_3$ | 2.14                  | 1.44                       |
| $X = F$ $Y = SiMe_3$ | 2.14                  | 1.44                       |
| $X, Y = CF_3$  | 2.27                          | 1.59                       |
| $X = CF_3$ $Y = F$ | 2.22                         | 1.53                       |
| $X = CF_3$ $Y = Me$ | 2.29                         | 1.61                       |
| $X = CF_3$ $Y = SiH_3$ | 2.23                         | 1.55                       |
| $X = CF_3$ $Y = SiMe_3$ | 2.25                        | 1.56                       |
| $X, Y = Me$    | 2.33                          | 1.65                       |
| $X = Me$ $Y = SiH_3$ | 2.24                        | 1.56                       |
| $X = Me$ $Y = SiMe_3$ | 2.24                        | 1.57                       |
| $X, Y = SiH_3$ | 2.22                          | 1.55                       |
| $X = SiH_3$ $Y = SiMe_3$ | 2.23                       | 1.56                       |
| $X, Y = SiMe_3$| 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-annelated benzopentalenes (THIOBENZPENT).

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

| Compound            | $\Delta E(S_1-T_1)_{va}$ |
|---------------------|--------------------------|
| 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”.

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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”.

References

S1 Grotjahn, R.; Maier, T. M.; Michl, J.; Kaupp, M. Development of a TDDFT-Based Protocol with Local Hybrid Functionals for the Screening of Potential Singlet Fission Chromophores. *J. Chem. Theory Comput.* **2017**, *13*, 4984–4996.

S2 Zeng, T.; Hoffmann, R.; Ananth, N. The Low-Lying Electronic States of Pentacene and Their Roles in Singlet Fission. *J. Am. Chem. Soc.* **2014**, *136*, 5755–5764.

S3 Zimmerman, Paul M.; Zhang, Zhiyong; Musgrave, Charles B. Singlet fission in pentacene through multi-exciton quantum states. *Nat. Chem.* **2010**, 2, 648–652.

S4 Johnson, Justin C.; Michl, Josef. 1,3-Diphenylisobenzofuran: a Model Chromophore for Singlet Fission. *Top. Curr. Chem.* **2017**, *375*, 80.

S5 Japhahuge, Achini; Zeng, Tao. Theoretical Studies of Singlet Fission: Searching for Materials and Exploring Mechanisms. *ChemPlusChem* **2018**, *83*, 146–182.

S6 Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions. *J. Chem. Phys.* **2006**, *125*, 144108.
Yamaguchi, K. Self-Consistent Field: Theory and Applications (Studies in Physical and Theoretical Chemistry); Carbo, R., Klobukoswki, M., Eds.; Elsevier Science: Amsterdam, 1990; p 727.