Elucidating the Relationship between Multiradical Character and Predicted Singlet Fission Activity

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ABSTRACT

The diradical and multiradical characters of a large and diverse set of 241 predicted singlet fission candidates are determined by multiconfigurational wavefunction methods, specifically natural orbital occupation number (NOON) analysis using the CASSCF method. The ascertained multiradical character strongly supports the current prediction that a good singlet fission candidate, independent of its structure, will tend to be of the weak biradicaloid class as well as having very little tetraradical character. Although the rule remains robust, it is not absolute as a small portion of our potential candidates are predicted to be closed shell. Additionally, a smaller handful of outliers with apparent tetraradical characters are identified, suggesting there may be the possibility, albeit rare, of singlet fission amongst weak tetraradicaloids.

INTRODUCTION

Singlet fission (SF) is a photophysical phenomenon in which a singlet excited molecule can impart some of its excitation energy to a neighbouring molecule, ultimately yielding two spin triplets *i.e.* $|S_0 S_1\rangle \rightarrow |T_1 T_1\rangle$. Once the spin-allowed triplet pair state is decoupled into two long-lived triplet excitons in, for example a photovoltaic device, the generation of four charge carriers could help surpass the Shockley-Queisser detailed

balance limit for single p-n junction solar cells (~33.7%).[1] There have been various efforts to prove that external quantum efficiencies exceeding 100% are possible experimentally,[2,3] with reports of devices achieving as high as 126%.[4] It can be shown that a solar conversion efficiency maximum of ~44.4% for a single-junction device, when an SF sensitizer is used, is theoretically possible.[5]

For a molecule to exhibit SF, there are a few criteria to satisfy; the most salient being the main energy criterion: $E(S_1) \geq 2 \cdot E(T_1)$ (although thermal activation is possible).[6] A second, important criterion is $E(T_2) \geq 2 \cdot E(T_1)$ such that triplet recombination *i.e.* the reverse process to SF does not readily occur.[7] The majority of organic molecules do not satisfy these criteria and, as a result, certain, specific molecular designs have been investigated, leading to a relatively small library of SF known materials.[7-9] The most important design principles are i) structural rigidity to avoid relaxation through conical intersections,[7] and ii) presence of a partial diradical character in the ground state.[8-11] For *de novo* design of a promising biradicaloid candidate one can, whilst considering chemical stability throughout, covalently perturb a perfect biradical in order to sample the energy surface before ultimately reaching an electronic arrangement in which the energy criteria are satisfied.[8] The typical oligoacenes such as tetracene and pentacene, which are strong candidates for SF, can be considered as mostly closed shell but do possess a weak diradical character in their ground states which can itself be adjusted by altering the number of rings,[12] or by heteroatom substitution.[13] It has been suggested that this necessarily weak, but non-negligible, to intermediate diradical character is a defining characteristic of efficient SF molecules.[14]

The idea behind this comes from a quantifiable correlation proposed by Nakano *et al*. using the valence configuration interaction two-site model.[15] It is found that the ground state diradical character of organic molecules and the energy level matching criteria for SF are not independent of one another. The diradical character (y_0) is defined by the occupation of the lowest unoccupied natural orbital (LUNO) and those compounds which satisfy a weak diradical character *i.e.* $y_0 > 0.1$,[16] appear to also have a natural electronic structure for effective SF.[17] It was also proposed that the tetraradical character (y_1), which is the occupation of the LUNO+1, ought to be sufficiently small *i.e.* $\frac{y_0}{y_1} > 5$,[18] for a molecule to possess the best electronic arrangement for efficient SF. The tetraradical index itself can still be relatively large *e.g.* $y_1 = 0.11$ for zeaxanthin (using PUHF),[19] as long as the ratio remains small, but clearly, the role of tetraradical character should be assessed considering on a broader set of examples. These indices together can yield the multiradical character (y_0, y_1) where for a closed shell molecule (0,0) is true, for perfect diradicals (1,0) and for tetraradicals (1,1) and is a useful metric to utilise when computationally searching for new SF molecules.

An unfortunate aspect of discovering new SF candidates with evident diradical character in their ground states is that, when they are eventually used for device fabrication, their likely chemical instability and propensity to react with other organic materials ultimately makes them unsuitable,[20] although current research into stabilisation via the captodative effect[11,21] and cross-conjugation[22,23] aims to alleviate this. Our previous work attempted to address this by testing, theoretically, a large set of known organic compounds with reduced or no pre-design,[24] similar to other high-throughput virtual screening efforts.[25-35] The 40K organic molecules were taken from the Cambridge Structural Database (CSD),[36] reduced from a total set of almost one

million structures. The outcome of the high-throughput screening yielded hundreds of novel structures which satisfy the main energy criterion $E(S_1) \geq 2 \cdot E(T_1)$ with optically active S_1. Since most of these structures are very different from those proposed earlier, they constitute an ideal new set to test existing design principles or encourage a shift of design perspective.

The goal of this work is to assess the ground state multiradical character of this large set of predicted SF candidates to determine whether the biradicaloid character is a prerequisite for the design of new SF molecules; these predicted candidates satisfy the main energy criterion computationally and are referred to as "potentially" or "predicted to be" SF active throughout the manuscript. We will also ascertain whether the exclusion of closed shell and tetraradicaloid molecules for SF can be justified.

METHODS

The structures will be chosen from the pool of 241 promising SF candidates from our previous high-throughput work in ref. 24. These are molecules with crystal structures deposited in the CSD and are depicted in the **Supporting Information**; they are predicted to satisfy the main energy criteria for SF after preliminary screening using X-ray geometries at the M06-2X/def2-SVP level as per a protocol benchmarked against reference CC2 calculations by Grotjahn *et al.*,[37] which is in agreement with an alternative benchmarking study by Brückner *et al.* for the TDDFT functional choice.[38] Additionally, the method is calibrated linearly using a sizeable set of ~100 molecules with experimental data, obtaining good correlations ($R^2 \sim 0.9$).[24] Together with the benchmarking and calibration, this protocol correctly evaluates the SF energy characteristic for well-known molecules such as tetracene and pentacene *i.e.*

endothermic for tetracene and exothermic for pentacene. 201 of these structures continue to fulfil the SF condition after a high-level geometry optimisation (BLYP35/def2-TZVP) and have optically bright first singlet excited states *i.e.* they have computed oscillator strengths of the first singlet state greater than 0.05. Those which fail to satisfy the main SF energy criterion after optimisation are kept in the initial round of CASSCF calculations to complement the trend, but no additional analysis is performed for them.

To quantify the diradical character of a molecule, it is possible to consider one or multiple methods and descriptors; one such method is NOON *i.e.* Natural Orbital Occupation Number analysis,[39] which utilises the occupations of the LUNO and LUNO+1 of a multiconfigurational wavefunction directly *e.g.* from a CASSCF calculation. The other way to assess the diradical character is to use a broken symmetry wavefunction method or spin-projected unrestricted HF/DFT.[40-43] One can include analysis of other descriptors such as the singlet-triplet gap $\Delta E(ST)$, spin density or N_{FOD} *i.e.* the integral over all the space of the fractional orbital density from finite-temperature DFT.[44-48] This work will focus only on results assessed by the NOON method using CASSCF as multiconfigurational methods are more naturally designed to describe fractional occupation numbers of orbitals. We note that diradical descriptors evaluated using PUHF may be different for the same molecule computed with CASSCF, however we have not investigated the structures using PUHF for comparison as it is not uncommon for triplet calculations to converge to an incorrect triplet state. For this reason, we could not find a reliable automatic way to ensure correct convergence of the broken symmetry wavefunction required by the PUHF for the large set.
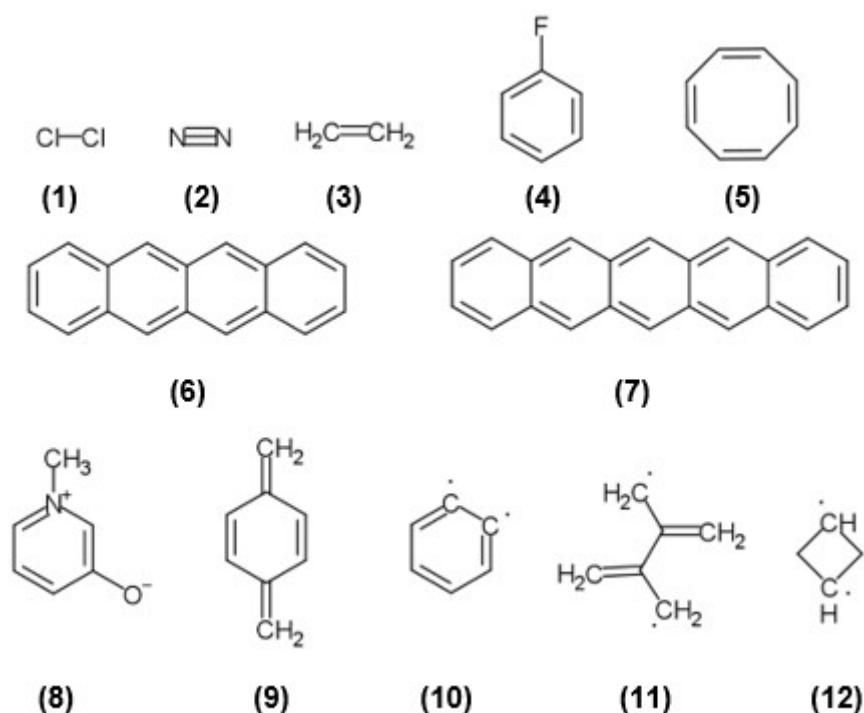
Figure 1 – Chemical structures of the twelve test set molecules

The CASSCF method normally requires manual, user intervention for each molecule and therefore does not naturally lend itself to a screening procedure. It is also sensitive to the choice of active space, hence, in order to feasibly evaluate the multiradical character for all 241 candidates, some compromises must be made. The initial set of calculations are performed using a fixed (6,6) active space invariably including (Hartree-Fock) orbitals from HOMO-2 to LUMO+2. Since the diradical and tetraradical indices fall within the HOMO-1 to LUMO+1 range, this active space is expected to suffice for most cases. It is useful to notice that no molecule in the set belongs to a non-abelian point group supporting degenerate orbitals. Such a shortcut method may lead to two distinct issues: the first is that orbitals with occupancies approaching two are kept although they could be considered fully occupied throughout

the calculation, therefore replacing them with other, more active orbitals may help accuracy and avoid instability. Furthermore, leaving the active space fixed may cause the additional issue in a situation where the orbitals at the periphery of the active space have appreciably small energy differences with the orbitals outside, and a bigger active space, or orbital swapping could be required.

This paper will focus on general trends (which should be visible despite potential inaccuracies) and exceptions to these trends, which can be studied individually at a higher level of detail, without the drawbacks mentioned above. The multiradical characters of the 241 structures which preliminarily fulfil the SF conditions can be assessed quantitatively by first calculating the HF orbitals of the previously optimised geometries using the 6-31G* basis set followed by CASSCF(6,6) with natural orbital analysis using the same basis set. Calculations were run with the Gaussian 16 software.[49] The quality of this protocol is tested on a set of twelve molecules (see **Figure 1**) including four closed shell, six biradicaloid and two biradical species: the results are given in **Table 1**. It can be shown that the method correctly ranks the diradical character of the sample considered and thus the method can be confidently used for the set of predicted SF candidates. The results in **Table 1** can also be used to identify a (soft) boundary between closed shell and biradicaloid molecules, which is typically method dependent and, for the current method can be set at around $y_0 = 0.09$. The indices y_0 and y_1, which are the occupations of the LUNO and LUNO+1 respectively, can be extracted from the one electron density matrix. For a subset of molecules displaying a greater deviation from the expected behaviour (low diradical character or high tetraradical character), the calculations have been repeated at the CASSCF(12,12) level to ensure the result remains consistent when the active space is doubled in size before concluding on its character.

Table 1 – Diradical character values for test set of molecules, ranging from closed shell to open shell biradicals.

Molecule	Class	CASSCF(6,6) y_0	CASSCF(12,12) y_0
1	closed shell	0.01	0.06
2	closed shell	0.06	0.07
3	closed shell	0.06	0.07
4	closed shell	0.08	0.09
5	biradicaloid	0.11	0.14
6[13]	biradicaloid	0.12	0.17
7[13,50]	biradicaloid	0.12	0.15
8[51]	biradicaloid	0.13	0.13
9[50,52]	biradicaloid	0.15	0.19
10	biradicaloid	0.16	0.16
11[53]	biradical	0.77	0.75
12	biradical	0.82	0.80

RESULTS AND DISCUSSION

As a first step, we will verify the hypothesis that SF activity is correlated to the diradical character of a molecule. To best capture this relationship, a scatter plot of the primary energy criterion versus the diradical index is given in **Figure 2** (E(S$_1$) and E(T$_1$) values are taken from our previous work in ref. 24). Our results support the current biradicaloid-focused direction regarding SF molecule design.[9,19,54-56] Those points close to E(S1) – 2·E(T1) ≥ 0 should be the best candidates for SF and do appear to have a weak diradical character. Those which generously satisfy the criterion (E(S$_1$) – 2·E(T$_1$) > 0.5), become more diradical, showing that SF is still possible for stronger biradicaloids but will, in general, be less efficient as alternative relaxation channels

may become more prevalent. The structures which, after geometry optimisation, no longer satisfy the condition *i.e.* $E(S1) - 2 \cdot E(T1) < 0$, do evidently look to be more closed shell as expected, though the points just shy of $E(S1) - 2 \cdot E(T1) \leq 0$ still belong to the main biradicaloid cluster (indeed, efficient endothermic SF is possible as is known with tetracene).[57] A reiteration of the SF/biradicaloid trend is given in **Figure 3**, similarly those points to the left (but closest) to the identity line ought to be the better candidates and have y_0 values in the weak biradicaloid range, whereas the closed shell structures lie further to the right of the line. An interesting point is to consider this typical result is now being shown for a large set of molecules and across a wide range of molecular classes that were outlined in our previous work, with SF known materials such as oligoacenes, cumulenes,[58] diketopyrrolopyrroles,[59] and also novel materials *e.g.* Pechmann dyes, Russig's blue analogues, silenes and others proposed in ref. 24. We note that there is some discrepancy in our absolute values of y_0 with other works *e.g.* we report the y_0 for tetracene as 0.12 at CASSCF(6,6) and 0.17 at CASSCF(12,12), whereas y_0 values exceeding 0.25 have been reported using the spin-projected Hartree-Fock (PUHF) method.[19,54]
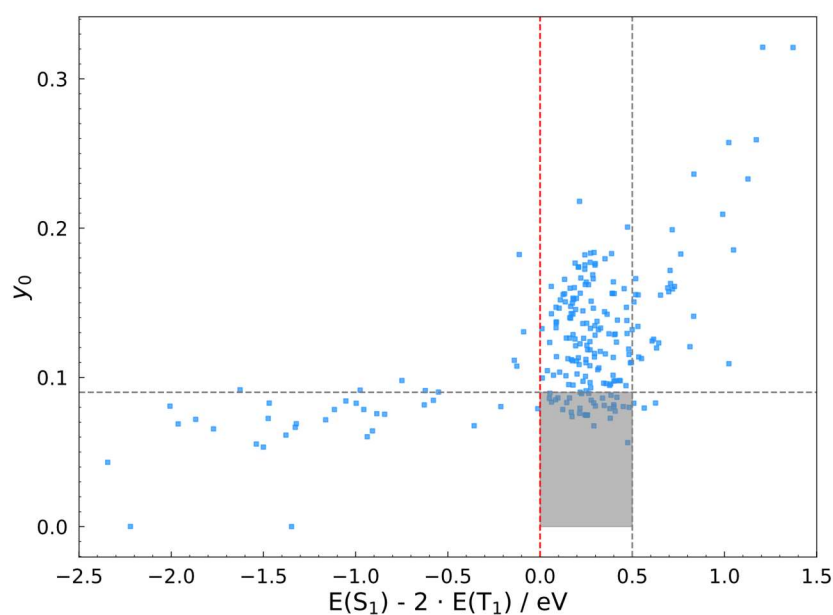
Figure 2 – Scatter plot of the SF primary energy criterion versus diradical index. The red dashed line is the cut-off for exothermic SF *i.e.* anything to the left of the line is no longer considered as a potential candidate. The horizontal dashed line is the boundary for closed shell and biradicaloid entries. The shaded grey area encapsulates the closed shell molecules which are predicted to exhibit efficient SF *i.e* to within 0.5 eV. The values for first singlet and triplet excited states are taken from our previous study in ref. 24.

This difference can be attributed to the use of NOON versus PUHF; larger values of y_0 when using PUHF is also observed elsewhere.[48] As long as the diradical character is compared with known benchmarks computed at the same level (*e.g.* data in **Table 1**) the trend in diradical character is consistent across methodologies.

Secondly, we give evidence of potentially SF active closed shell molecules as there are a handful of interesting cases, with some appearing in groups, which can be considered closed shell according to our protocol, but still fulfil the SF condition favourably.
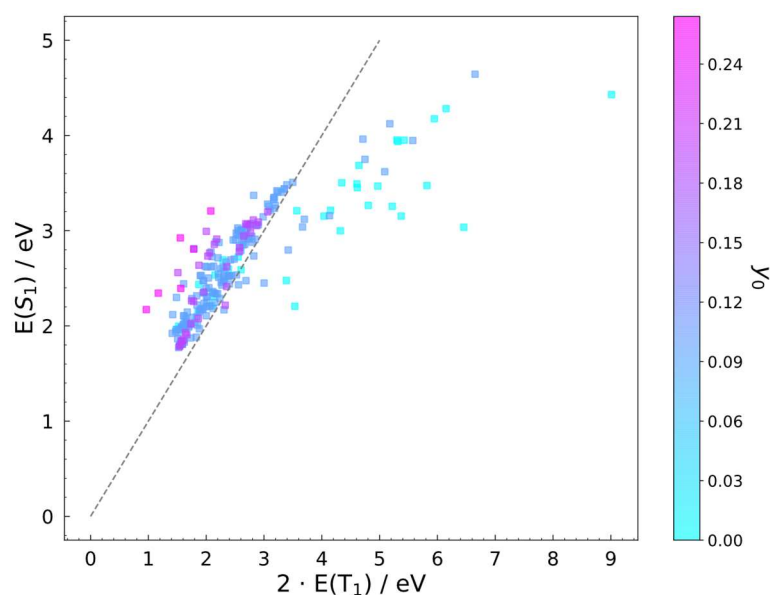
Figure 3 – Scatter plot of twice the first triplet excited state energy versus the first singlet excited state energy, colour coded with the diradical index. The dashed identity line is the cut-off for exothermic SF *i.e.* anything to the right of the line is no longer considered as a potential candidate.

There are 37 molecules (shaded in grey in **Figure 2,** with structures provided in the **Supporting Information**) which are computationally predicted as SF active ($0 < E(S1) - 2 \cdot E(T1) < 0.5$), but fall into the closed shell regime ($y_0 < 0.09$). For example, a group of six sidechain substituted pentacene derivatives (see **Figure 4**), including SF active TES-pentacene,[60] all yield y_0 values of ~0.07 which would indicate a closed shell character when compared with the results in **Table 1.** As the molecules share the same chromophore as pentacene, their diradical character ought to be similar to pentacene ($y_0 = 0.12$ using CASSCF(6,6)), but the deviation in the general case could be justified by the possible electronic effects of sidechain substituents. Along with these molecules, there are other pentacene derivatives, without including heteroatom substitution, which range from $y_0 = 0.10$ to 0.16.
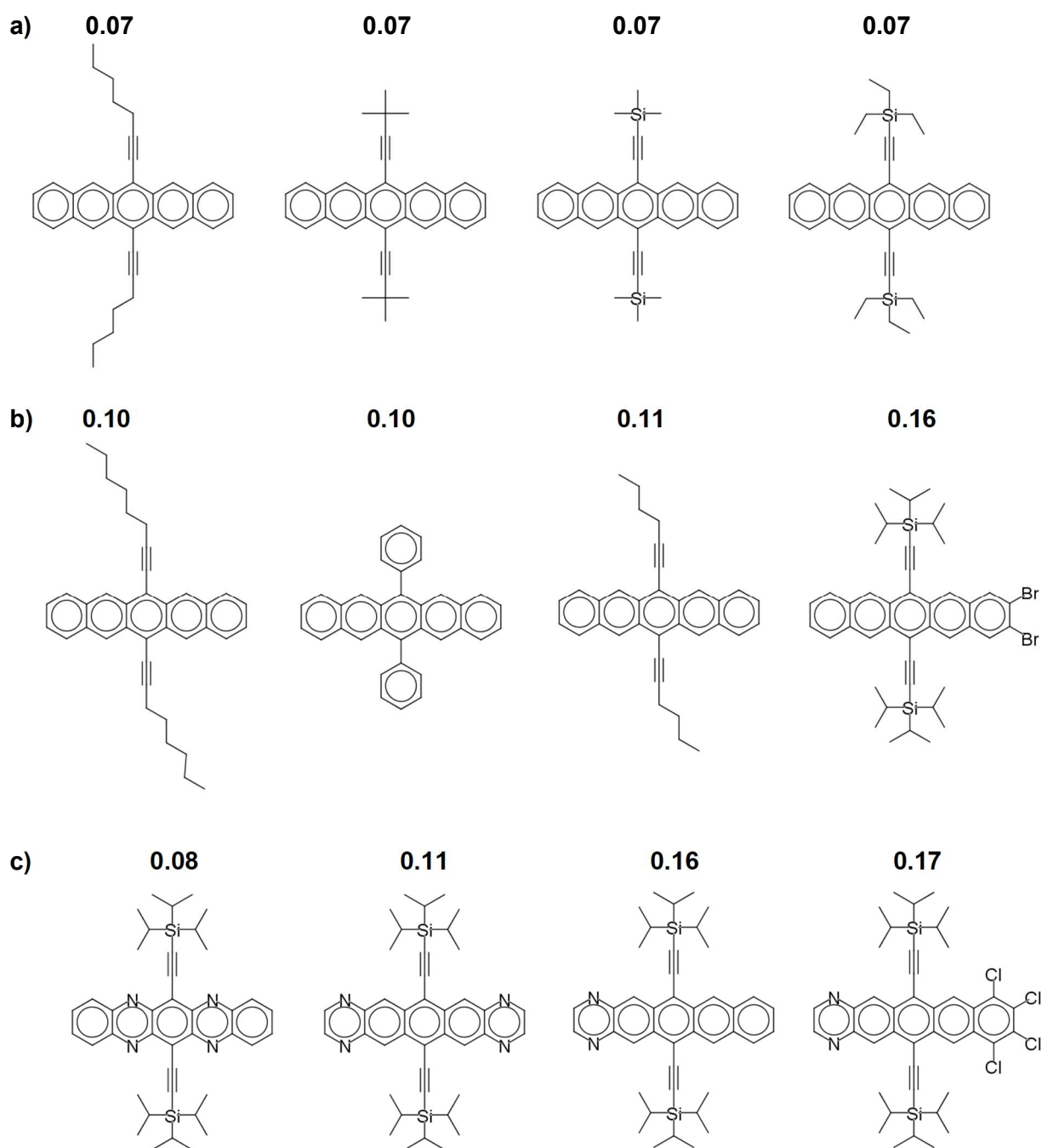
Figure 4 – a) Chemical structures of four of the pentacene derivatives with diradical indices equal to 0.07, b) pentacene derivatives with larger diradical indices c) chemical structures of N-doped pentacene derivatives. The diradical indices are evaluated at the CASSCF(6,6) level and labelled above each structure.

If this is an effect due solely to the computational method, it is important to consider the sensitivity of these calculations to minor side-group substitutions on the molecules at the boundary of closed shell to biradicaloid. It can also be noted that the effect of heteroatom substitution in ref. 13 is similarly observed for a small number of our entries *i.e.* the diradical character of pentacene derivatives increases markedly with nitrogen substitution into the outer rings and less so when doped into the inner rings; asymmetric nitrogen substitution appears to further increase the ground state diradical character in these examples. To confirm the existence of closed shell, potentially SF active molecules in our set, we have recomputed the multiradical indices for the 37 entries at CASSCF(12,12) level. From this, the number of closed shell candidates ($y_0 \leq 0.09$) is reduced from 37 to only 10, with the pentacene derivates described in **Figure 4** showing an increased diradical character (see **Table S1**).
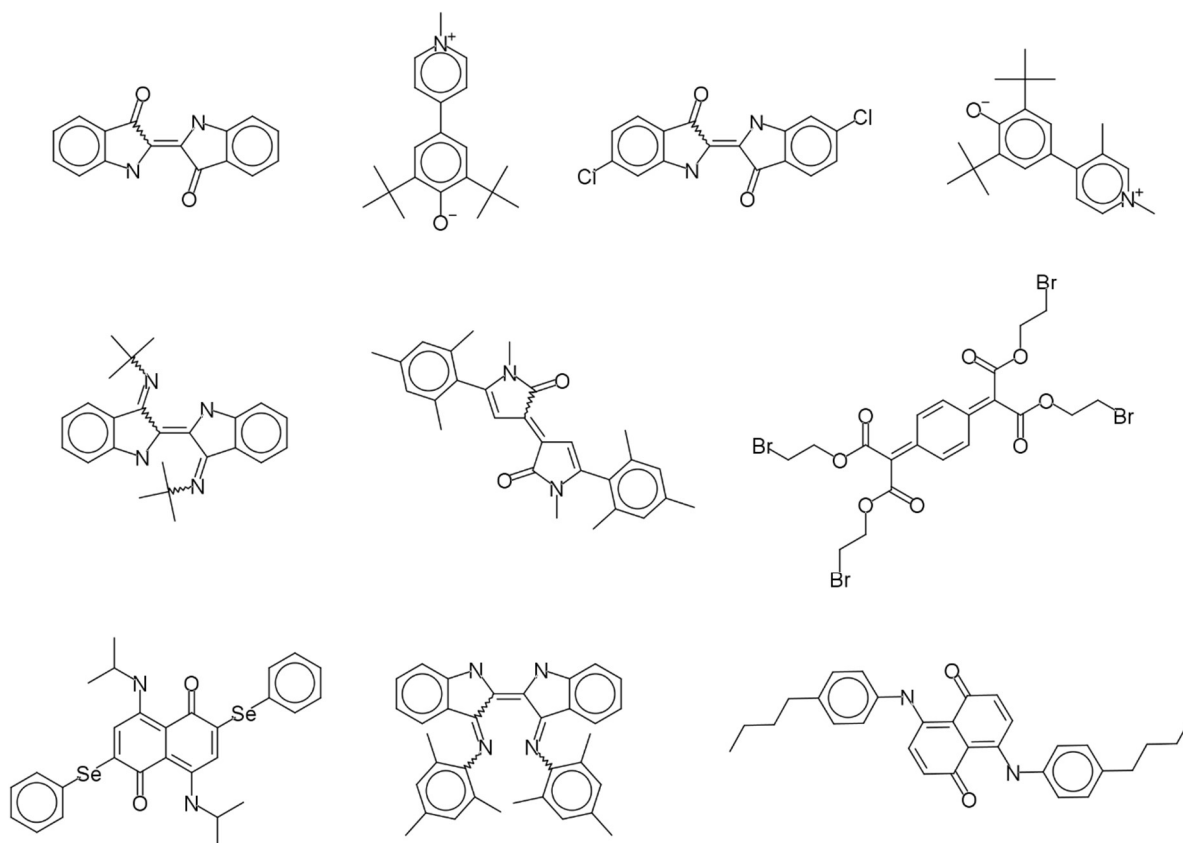
Figure 5 – Chemical structures of remaining closed shell molecules *i.e.* $y_0 \leq 0.09$ after using CASSCF(12,12).

It must be said, however, that most of the structures remain closer to the soft boundary for biradicaloid character. The median y_0 for these structures recomputed with a (12,12) active space is 0.11 and their closed shell status should not be completely ruled out. The 10 molecules which should be labelled as closed shell but are still computationally predicted to be SF active are illustrated in **Figure 5**. The set comprises molecules that are known to undergo SF like indigo derivatives,[61] and novel molecules such as substituted pyridinium phenolate and aminonaphthoquinone. A closed shell molecule could satisfy the SF criteria by having a sufficiently large exchange interaction, something that may take place also in the absence of diradical

character if the excited state involves the excitation between orbitals very localized in the same region of space.
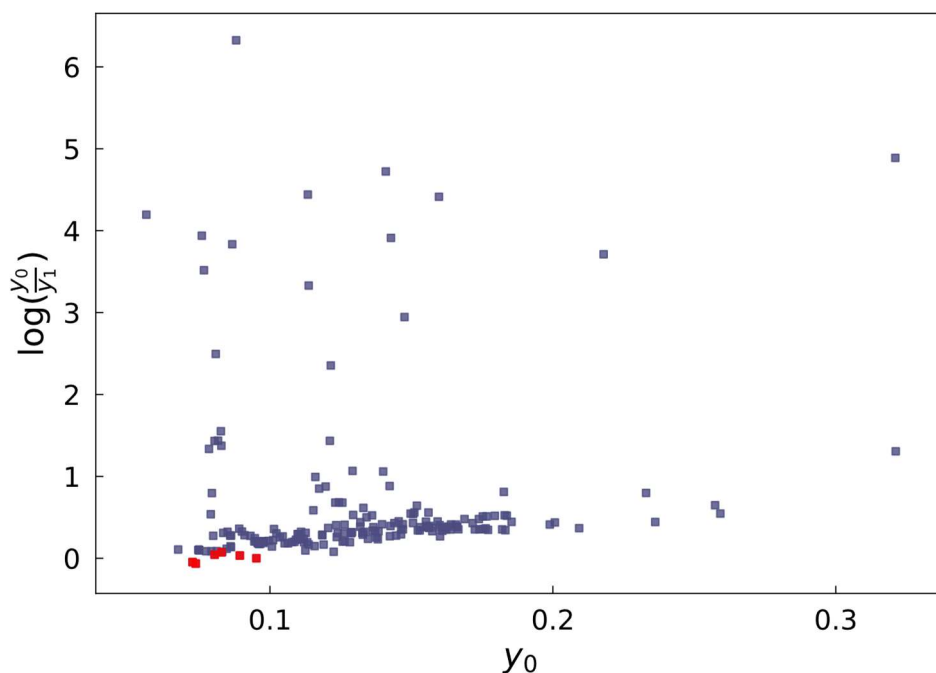

Figure 6 – Scatter plot of the diradical index and the logarithmic ratio between diradical and tetraradical indices to better describe the multiradical character. Points marked in red show the six molecules with extreme tetraradical character.

These results can be seen to confirm the current view that a moderate diradical character increases the propensity of molecules to be SF active but the exceptions to the rule still involves about 10% of the molecules considered. When this observation is combined with the fact that all biradicaloids appear to be SF molecules we can conclude that designing molecules with biradicaloid character is definitely a successful strategy but, by imposing this condition, a fraction of promising candidates may be mistakenly ignored. Indeed, if one wishes to discover SF materials with improved

chemical stability, the molecules with lower diradical character *i.e.* the *exceptions* to the rule, may constitute particularly interesting starting points.

Lastly, we provide evidence of potential tetraradicaloids which are computationally predicted to be SF active, somewhat contrary to the commonly accepted view in literature.[16,19,40] **Figure 6** describes the distribution of multiradical character in the set considered and highlights the six molecules with the highest tetraradical character that we consider for a more detailed study.

Table 2 – Multiradical values for the weakly tetraradical molecules, given at the CASSCF(6,6) and CASSCF(12,12) levels.

Molecule	CASSCF(6,6)		CASSCF(12,12)	
	y_0	y_1	y_0	y_1
13	0.095	0.095	0.11	0.11
14	0.074	0.085	0.092	0.099
15	0.089	0.083	0.091	0.083
16	0.083	0.070	0.098	0.077
17	0.073	0.081	0.184	0.076
18	0.080	0.073	0.185	0.067

For these molecules, the absolute values of y_0 and y_1 are still small but of comparable magnitude. To ensure the tetraradical character is preserved once the active space and thus accuracy are increased, these six molecules are recalculated using CASSCF(12,12). The results are given in **Table 2** with the structures of the molecules it refers to illustrated in **Figure 7**. It can be shown for some entries that the value of y_0 is increased whilst the value of y_1 remains relatively constant allowing them to better

obey the biradicaloid condition: this is the case for molecules **17** and **18**. The most interesting molecules of the set are then **13**, **14**, **15** and **16** which maintain a $\frac{y_0}{y_1}$ ratio indicative of a sizeable tetraradical character after the active space is increased.
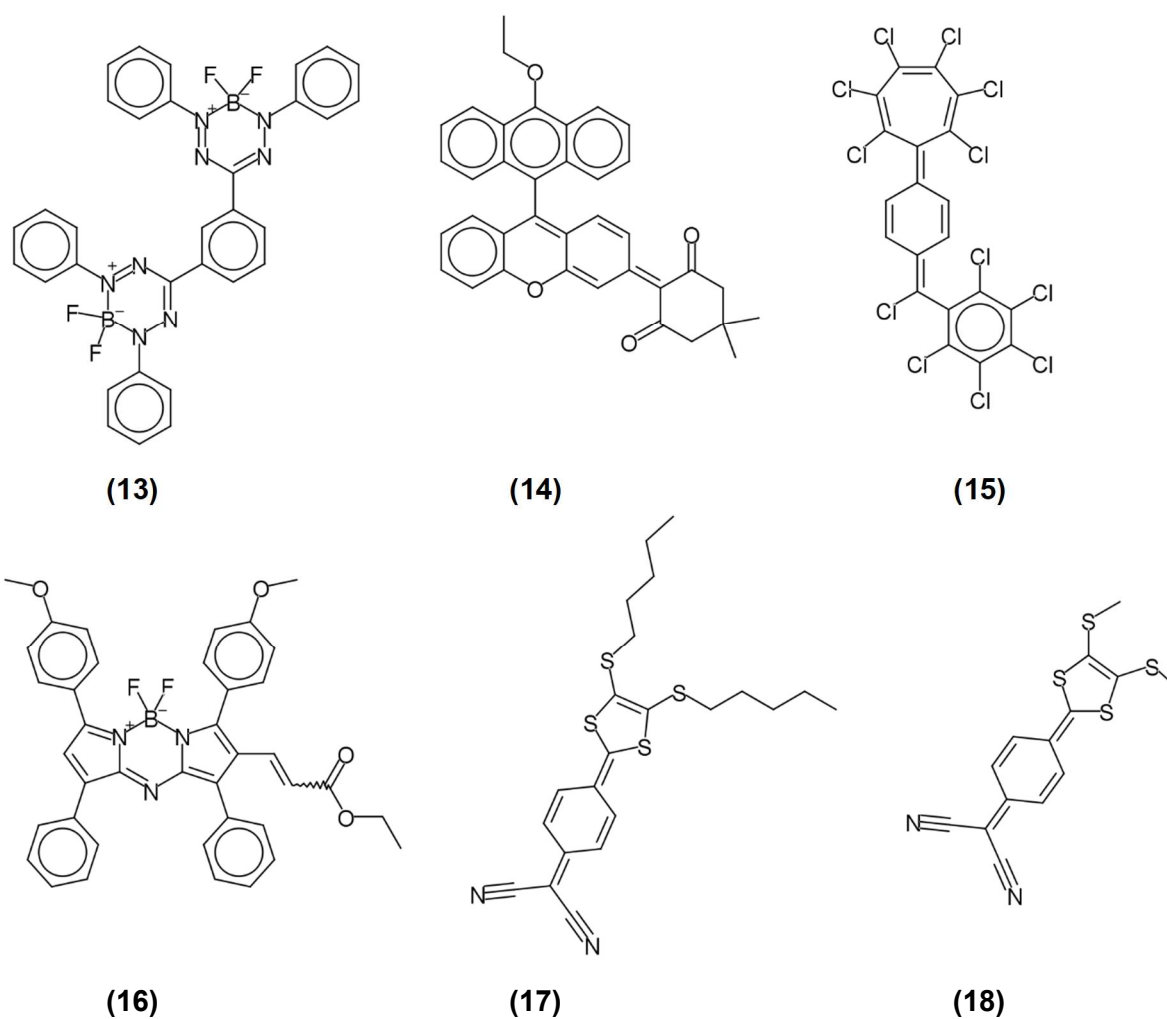

| (13) | (14) | (15) |
| (16) | (17) | (18) |

Figure 7– Chemical structures of molecules with notable tetraradical characters and are predicted to satisfy the main SF energy criterion (to within 0.4 eV).

These molecules share structural similarities between them, such as the two azaBODIPY style structures (**13** and **16**) and the two TCNQ-esque structures (**17** and **18**), and in fact some azaBODIPY and TCNQ derivatives are thought to be SF active

experimentally.[62,63] It is clear from the structures that the presence of a tetraradical character amongst predicted SF compounds is distributed across the chemical space and is not related to a specific chromophore *i.e.* there are other azaBODIPY derivatives within our dataset which do belong to the biradicaloid class. Since these are only a handful of suspicious entries in a set of 201 satisfactory molecules, the evidence for exothermic SF in a tetraradicaloid cannot be considered conclusive but should warrant further investigation, especially since all of them fall within the efficient SF energy range *i.e.* $0 < E(S_1) - 2 \cdot E(T_1) < 0.5$ eV.

CONCLUSION

In conclusion, we have shown that there is an inherent biradicaloid character associated with many organic molecules which plainly satisfy the electronic criteria needed for SF by testing on a large and statistically significant set of molecules. This suggests that molecules which happen to host the, otherwise rare, electronic arrangement will have a high likelihood to also exhibit some diradical character and will suffer the destabilisation associated with it. The previously predicted relationship between the propensity for SF and biradicaloids remains robust, hence the future search for SF candidates cannot escape the consideration of biradicaloids. However, there are exceptions with around 10% of the structures satisfying the main energy criterion whilst being considered closed shell alongside another 2% of SF satisfactory tetraradicaloids. Evidently, the rule is not absolute when considering only the main energy criterion for SF, so even though a design based search focusing only on biradicaloids will naturally find SF active molecules, it will inevitably miss the rarer but more stable closed shell counterparts, along with potentially interesting tetraradicaloids. Since there is difficulty in quantifying the multiradical character itself

due to the merits of each method and the relatively large number of eligible descriptors, it is necessary to investigate select candidates further with different methods, higher levels of theory and ultimately experimentation, whilst also considering a wider electronic structure for each molecule.

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