

Singlet Fission Molecules among Known Compounds:

Finding a Few Needles in a Haystack

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Abstract

A large set of candidates for singlet fission, one of the most promising processes able to improve the efficiency of solar cells, are identified by screening a database of known molecular materials. The screening was carried out through a procedure exploiting quantum chemical calculations of excited state energies, carefully calibrated against a substantial set of experimental data. We identified ~200 potential singlet fission molecules, the vast majority of which were not known as singlet fission materials. The molecules identified could be grouped into chemical families enabling the design of further singlet fission materials using the hits as lead compounds for further explorations. Many of the discovered materials do not follow the current design rules used to develop singlet fission materials illustrating at the same time the power of the screening approach method and the need of developing new design principles.

Broader Context

Only a handful of molecular materials are known to undergo *singlet fission*, i.e. once excited in a singlet state by radiation they produce two triplet excitons of about half the excitation energy. This process was proven able to improve the efficiency of different types of solar cells and has been proposed for a range of optoelectronic applications. Expanding the range of available singlet fission materials is considered essential for all applications and it is the only way to improve stability, processability, chemical and electronic compatibility with the other device components. We show here that there are *hundreds* of compounds that are known, chemically stable and characterized in the solid state which satisfy all the energetic criteria for singlet fission to take place. We identify them among the million structures deposited in the Cambridge Structural Database by devising an efficient computational screening procedure calibrated against an ample set of experimental data.

Singlet fission can be described as an electronic transition where a singlet state (e.g. S_1 , typically generated by excitation from ground state) is converted into two triplet excited states (T_1). This transition involves invariably at least two molecules (or molecular fragments) and the two triplets in the final state are localized in different regions of space, e.g. on two different molecules.¹ The transition is spin allowed, i.e. the state formed from the initial excited state is a multiexcitonic state where the two triplets are combined into an overall singlet (1TT) that can later dissociate into separate triplets according to the scheme $S_1 + S_0 \rightleftharpoons ^1TT \rightleftharpoons T_1 + T_1$.^{1, 2} The enormous interest for singlet fission today is motivated by its potential applications in photovoltaic technologies. Through singlet fission a photon can generate two long lived excited states. One of the assumptions for the derivation of the thermodynamic limit of a single-junction solar cell, known as the Shockley-Queisser limit, is that a single photon can generate only one excited state (an electron-hole pair). A device able to generate two excited states per photon may be able to overcome this assumption and opens a path to increased efficiency, e.g. producing more energy under solar irradiation.³ However, no device is currently able to overcome all assumptions obtained for the derivation of such limit. Devices employing singlet fission materials have been demonstrated for organic solar cell⁴ and are being explored with silicon, perovskites and dye sensitized solar cells.⁵

Virtually all overviews of the topic presented in literature^{2, 6} state *the same single main limitation* in this research area: *there are just too few materials undergoing singlet fission*. All proposed technologies require the integration of singlet fission materials with other components and solving all experimental problems related to chemical stability, processability and alignment of energy levels becomes impossible if the library of candidates is so limited. Also the chemical physics of singlet fission is not fully understood because of the small number of materials: photophysical measurements can be explained by multiple theoretical models^{7, 8, 9, 10} and the only way to adjudicate between different explanations is through a broader set of materials.

An obvious requirement for singlet fission to take place is for the singlet state energy to be more than double the triplet state energy, e.g. $E(S_1) \geq 2E(T_1)$. This condition is normally not satisfied and the focus of most authors has been to design molecules with sufficiently small triplet energies. There is essentially only one design rule that has been put forward in slightly modified forms by several authors: a low triplet energy is associated with molecules with *a strong biradical character in the ground state (biradicaloids)*.¹¹ Elegant proposals have been put forward combining intuition and electronic structure calculations to design molecules displaying strong biradical character in the ground state.¹²⁻¹⁴

There are however additional considerations suggesting that the search for novel singlet fission materials should be expanded. First of all, biradicaloids tend to be chemically unstable (they undergo Diels-Alder addition to other unsaturated compounds because of the (partially) unpaired electrons) making them often incompatible with other organic materials.¹⁵ Molecules designed to be potentially unstable are not the most attractive targets for the synthetic chemists especially because the ability of stabilizing such molecules in solid form is hard to predict theoretically. Furthermore, there are additional conditions that needs to be satisfied by singlet fission materials (having bright excited

singlet states, $E(T_2) > 2E(T_1)$ to avoid triplet-triplet fusion, rigidity to avoid intersystem crossing to the ground state, and others²⁾ which, once appropriately weighted, should also form the basis for the search. Finally, since singlet fission involves electronically coupled molecules, it would be desirable to have also information on the molecular packing to predict the propensity toward singlet fission.¹⁶

To address at once all the problems above we identify in this work potential candidates for singlet fission in a database of known molecular materials, the Cambridge Structural Database (CSD).¹⁷ We will look at molecules that have been prepared for various purposes and characterised in their crystalline form, but might not have been tested as organic semiconductors, and check computationally whether they could be singlet fission active. Of approximately one million crystal structures in the database in September 2018, we limited our attention to the molecules whose crystallographic structure does not include metals and have only one type of molecule with less than 100 atoms per molecule. This set of 250K materials contains in large part materials that are not semiconductors and will not be considered further. Single point semi-empirical and low-accuracy DFT calculations have been used to define a subset of the CSD containing only semiconductors, i.e. with (approximate) band gap not exceeding 4 eV (see detail in the Supporting Information (SI)). Within this set of 40K materials we looked for suitable candidates for singlet fission.

Before devising a suitable screening procedure we should verify that we have a method sufficiently accurate for the computation of the excitation energy of singlet and triplet states in a large number of molecules. Such method will determine the quality of the final predictions and enable the definition of more approximate computational schemes. We have chosen one of the methods proposed in ref. ¹⁸, consisting of a geometry optimisation with a large basis set (BLYP35/def2-TZVP), followed by TDDFT calculation of the excited state (M06-2X/def2-TZVP), to evaluate the vertical excitation energy to states S_1 and T_2 and a Δ SCF procedure (M06-2X/def2-TZVP), to evaluate the excitation energy to T_1 (see SI). While wave-function methods are needed to study the process of singlet fission in molecular *dimers*,¹⁹ they are computationally more demanding than DFT-based methods and unsuitable for large scale screening. On the other hand, the computation of the excited energy of *isolated molecules* is sufficient to screen out the vast majority of the candidates and the accuracy of such excited state calculations is the one to be assessed.

We have then constructed a large database of 100 singlet and triplet experimental excitation energies using data from literature²⁰ (the database with detail of each entry is available in the SI). The comparison between experimental and computational data is shown in Figure 1. The proposed methodology, already fairly accurate in the absolute terms, can become very predictive if the comparison between experimental and computed excitation energy is used to calibrate the prediction for new set of molecules. It should be noted that this calibration effort is complementary to the others in literature^{21, 22} that have not considered states of different multiplicity and enable a robust determination of the confidence level. Further tests in the supporting information demonstrate that both the screening *and* the *final results* are robust against the choice of density functional, provided it contains exact exchange interaction to describe accurately the triplet state.

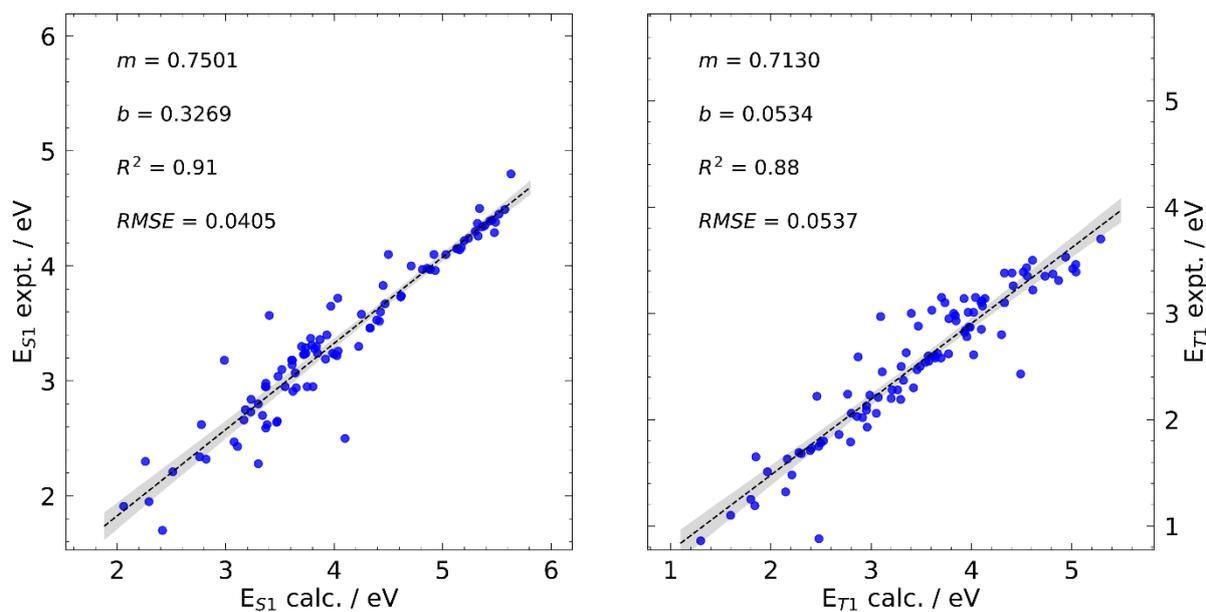


Figure 1. Comparison between calculated (M06-2X/def2-TZVP) and experimental S1 (left) and T1 energies (right). Shaded areas represent a 95% confidence interval. We calibrated calculations to experimental data with a linear fit (*i.e.* $y = mx + b$), and we provide two metrics for the quality of the fit (square correlation coefficient, R^2 , and root mean squared error, RMSE).

The method calibrated in Figure 1 is computationally too time consuming to be applied to 40K molecules. We therefore perform a *preliminary screening* of the data set performing single point calculations *at the molecular geometry derived from X-ray diffraction* with the same method and a reduced basis set (def2-SVP). For this initial step we have considered only the primary criterion for singlet fission:

$$E(S_1) \geq 2E(T_1). \quad (1)$$

As one can see from Figure 2 (left), only a small minority of data points satisfy condition (1). We assign these entries to group A (419 molecules), deserving an in-depth investigation. Molecules that miss the criterion by less than 0.4 eV are retained in group B (641 molecules), to be analysed in future work and all the others are labelled as belonging to group C and not considered further. To limit the predicted singlet fission molecules to those that can be characterized more easily and can be used in the current applications we added the condition that state S_1 is optically bright (*i.e.* the computed oscillator strength is larger than 0.05), and that the energy of the triplet is not too low, *e.g.* $E(T_1) \geq 0.4$ eV. The 262 molecules in group A satisfying these additional criteria have been subjected to accurate optimization and excited energy calculations.

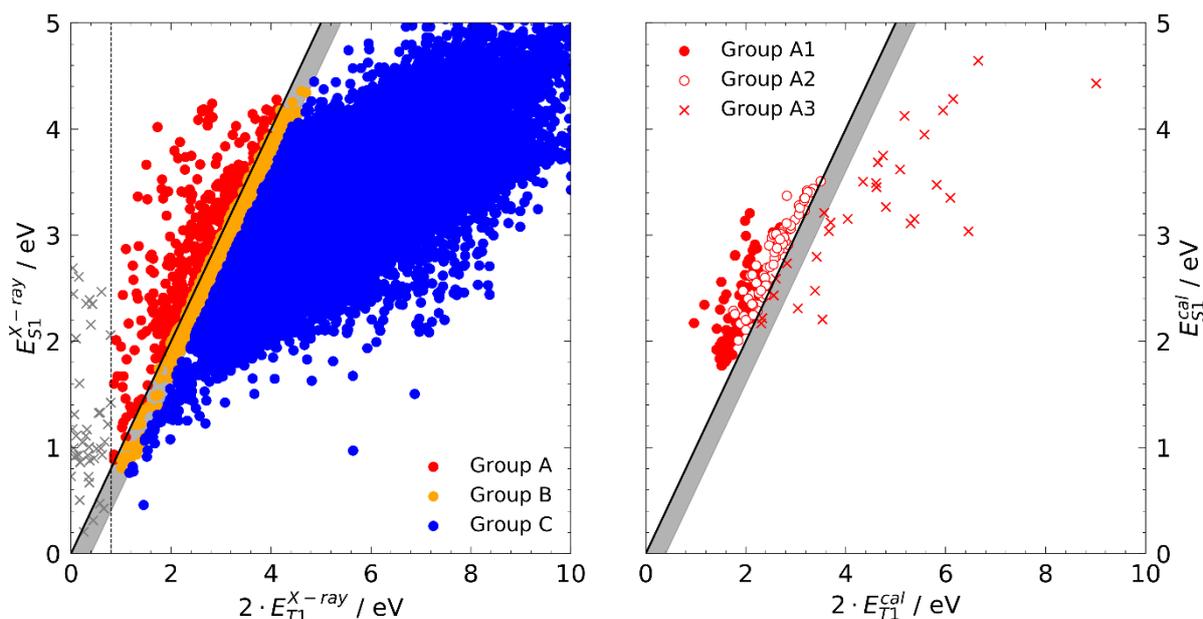


Figure 2. (left) Results of the screening on the x-ray geometries of 40K molecules. The solid black line indicates the decision boundary. The grey shaded area identifies group B. The thin dashed black line is the boundary for molecules with too low triplet energies, shown as grey crosses. (right) Results of accurate calculations: empty symbols identify molecules not satisfying the secondary criterion.

Figure 2 (right) illustrates graphically the results of the accurate calculations. The energy levels for the evaluation of criterion (1) have been adjusted according to the calibration shown in Figure 1. One can notice that a small fraction (18%) of the molecules that satisfied criterion (1) in the preliminary screening do not satisfy it in the accurate calculations, we label them as belonging to group A3. This relatively small fraction justifies, a posteriori, the use of the approximate method for the initial screening of the 40K molecules. The molecules that satisfy criterion (1) are further separated into a subgroup A1 (full symbols in Figure 2) that satisfy also the secondary criterion for singlet fission:²

$$E(T_2) \geq 2E(T_1) \quad (2)$$

and a subgroup A2 (empty symbols in Figure 2) not satisfying criterion (2). Approximately 45% of the molecules satisfy criterion (1) but not criterion (2), mostly molecules with relatively higher $E(T_1)$. Considering that criterion (2) cannot be verified experimentally and is associated to larger computational inaccuracies it is reasonable to use it for classifying the final results rather than removing potential entries in the preliminary screening.

The number of candidates satisfying criteria (1) and (2) or only (1) is sufficiently large that one can perform a chemical classification of the molecules predicted to be excellent singlet fission materials and already extract new chemical insights. The 213 molecules in group A1 and A2 have been divided into 16 chemical families as illustrated in Figure 3, including the number of instances in each family and an example. The first seven families contain compounds well known to undergo singlet fission or that have been considered for it either theoretically or experimentally, e.g. (1) structure related to para-quinone like TCNQ, (2) pentacene derivatives and analogues, (3) other polyacenes, (4) polyenes, (5) cumulenes,²³ (6) azadipyrin derivatives²⁴ and (7) indigo analogues.²⁵ The following eight families

contain compounds that, to the best of our knowledge, have not been considered for singlet fission, namely (8) benzofuroxan derivatives, (9) derivatives of quinoxaline (or pyrazine) 1,4 dioxide, (10) derivatives of 1-5,dioxynaphthalene, (11) Pechmann dyes, (12) Russig's blue analogues, (13) azo-benzene dioxide analogues, (14) isatogen analogues and (15) Silenes. At least three examples from each of the families (8)-(15) are predicted to be singlet fission materials. The remaining 85 molecules could not be classified and are assigned to "family" (16) with five examples given in Figure 3. These latter compounds, especially the chemically simpler one, can be considered useful lead compounds to develop new sets of singlet fission materials. Almost all of the unclassified compounds are not known as singlet fission materials. It is also interesting to note that, for some of the examples, e.g. the silenes or the first molecule of family (16) reported in Figure 3, it is not easy to write a biradical valence bond structure. In other words, the existing design rule would have missed some of the relevant molecules and the set of molecules in group A can be used as a starting point to expand the current understanding of structure-property relationship for singlet fission.

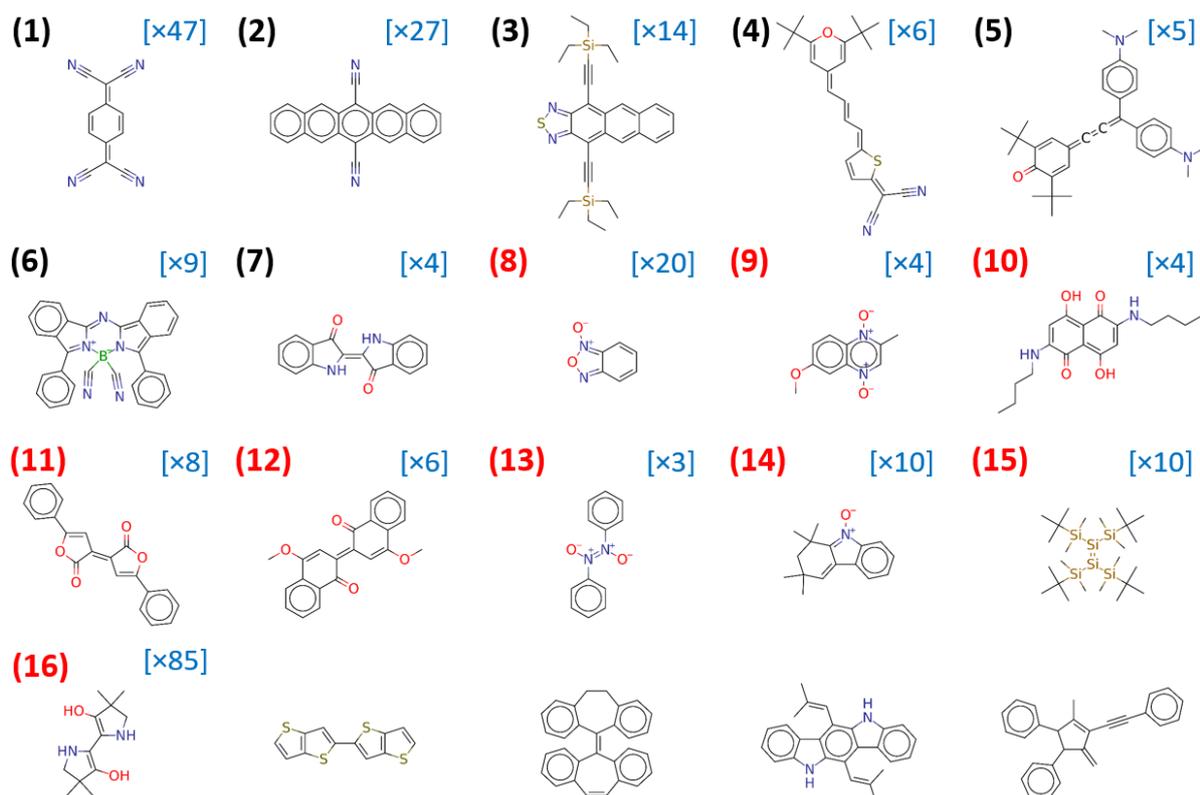


Figure 3. Examples of singlet fission molecular materials identified through screening (chemical name given in the main manuscript). (1)-(7) are representatives of different chemical families known or hypothesized in literature to undergo singlet fission. (8)-(15) are representatives of chemical families previously not associated with singlet fission properties. The five elements in group (16) are examples of molecules that could not be associated to a particular chemical family. The number of elements in each group satisfying the main energetic criterion is also given in square parentheses.

In the selection of materials for further applications, several additional considerations can be made. We have considered vertical energy differences rather than adiabatic (energy differences between minima of the potential energy surface). As illustrated in the SI, and largely expected, considering minima makes it more likely to satisfy criterion (1), i.e. the range of potential candidates can be further expanded. Moreover, among the most studied singlet fission materials we find several, like tetracene, that narrowly miss criterion (1). A condition for singlet fission to be ultrafast and beat alternative relaxation channels could be set as $E(S_1) \approx 2E(T_1)$, i.e. generously meeting the energy criterion (1) could be counterproductive. Furthermore, one could in principle exploit the information on the molecular packing contained in the CSD to select materials with favourable dynamics of formation of the 1TT states on the basis of the non-adiabatic coupling between the relevant states.² This is at the moment very challenging in a material screening perspective for different reasons. Many authors¹⁹ recommend performing such calculations using wavefunction-based methods, which are unsuitable for screening because of the computational cost and their greater complexity. Even if faster methods based on DFT can be introduced,²⁶ the non-adiabatic coupling in the crystal structure can be misleading by itself: in the equilibrium structure of rubrene singlet fission is symmetry forbidden and promoted by exciton-phonon coupling,²⁷ which is computable only for few materials at the time.²⁸

In conclusion, we have shown that there are hundreds of molecules that are well characterized and satisfy the energy criteria for singlet fission. Such molecules remain rare but they span a chemical space much broader than previously thought and, in some instances, outside the currently accepted design rules. Our results constitute a starting point for a renewed search for alternative singlet fission materials: simpler analogues can be identified among commercially available compounds and quickly tested experimentally, and the chromophores can be chemically functionalised to fine-tune the energy of singlet or triplet excited state.

Supporting Information Available. (i) Computational details; (ii) Details on generating a dataset of molecular semiconductors from the CSD; (iii) Comparison between the results obtained with different density functionals; (iv) Comparison between adiabatic and vertical excitation energies; (v) Database with raw data needed to reproduce figure 1 in the main manuscript; (vi) Database of molecules in groups A1-A3 and their optimized geometries; (vii) Database of molecules in group B. Electronic data can be downloaded from <https://bitbucket.org/dpadula85/singlet-fission-screening>.

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