

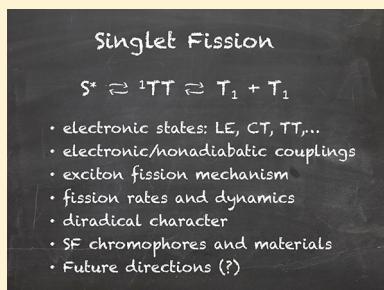
## Theoretical Modeling of Singlet Fission

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**ABSTRACT:** Singlet fission is a photophysical reaction in which a singlet excited electronic state splits into two spin-triplet states. Singlet fission was discovered more than 50 years ago, but the interest in this process has gained a lot of momentum in the past decade due to its potential as a way to boost solar cell efficiencies. This review presents and discusses the most recent advances with respect to the theoretical and computational studies on the singlet fission phenomenon. The work revisits important aspects regarding electronic states involved in the process, the evaluation of fission rates and interstate couplings, the study of the excited state dynamics in singlet fission, and the advances in the design and characterization of singlet fission compounds and materials such as molecular dimers, polymers, or extended structures. Finally, the review tries to pinpoint some aspects that need further improvement and proposes future lines of research for theoretical and computational chemists and physicists in order to further push the understanding and applicability of singlet fission.



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Special Issue: Theoretical Modeling of Excited State Processes

Received: October 1, 2017

Published: April 12, 2018

## 1. INTRODUCTION

Singlet fission is a photophysical reaction typical of some organic compounds where an excited singlet state evolves into two spin-triplets. The singlet fission process has been known and studied since 1965,<sup>1</sup> but the interest toward this phenomenon has grown very rapidly in the last years; we have recently seen an explosion in the number of publications devoted to the study of singlet fission. Among the multitude of investigations, theoretical and computational efforts have played a crucial role in the advance of the field, providing a much deeper knowledge of this peculiar photophysical phenomenon. In particular, computational studies have been decisive in understanding the most relevant factors for the efficiency of singlet fission, the properties of the electronic states involved, the potential fission mechanisms, the key parameters controlling fission rates, and the most important features regarding the dynamics of the reaction. Despite these advances, there is still much work that needs to be done in order to fully comprehend singlet fission and to have singlet fission materials integrated into efficient solar cells able to compete with other solar energy sources.

This review presents and discusses the most significant advances regarding the theory and computational simulation of singlet fission with special interest in the advances achieved since the (excellent) reviews in the field of singlet fission done by Smith and Michl.<sup>2,3</sup> The present work aims to highlight some of the most relevant aspects of the field and update the theoretical understanding of singlet fission, overview the state-of-the-art computational methodologies employed for its study, and gather the main results obtained since 2013. Although the manuscript cites many of the recent studies on singlet fission, it does not pretend to be an exhaustive recollection of all the extensive work done.

### 1.1. Historical Perspective

The origins of singlet fission date back to the early works of Singh on the photophysical processes in anthracene crystals.<sup>1,4,5</sup> In 1963, Singh and Stoicoff identified a dark intermediate state able to simultaneously absorb two photons not present in the free anthracene molecule.<sup>5</sup> Two years later the same authors characterized this intermediate as a high-energy  ${}^1A_g$  state formed as two coupled triplet excitons that can either dissociate, which constitutes the first known reference to the singlet fission process, or relax to the lowest excited (bright) singlet.<sup>1</sup> In 1968, Swenberg and Stacy proposed the bimolecular decay of a singlet exciton into a pair of triplet excitons in tetracene crystals<sup>6</sup> in an attempt to explain its surprisingly low fluorescence quantum yield.<sup>7</sup> In their pioneering work appears the first rate expression used to evaluate the kinetics of singlet fission. In 1969, two separate works presented experimental evidence, based on the dependence of fluorescence intensity with an applied magnetic field, of the singlet fission process in crystalline tetracene,<sup>8,9</sup> confirming the theoretical predictions done by Swenberg and Stacy. In 1970, the existence of the intermolecular correlated triplet-pair state was also hypothesized as an intermediate for the triplet–triplet annihilation process in anthracene crystals.<sup>10</sup> Subsequent works were devoted to the development of the exciton fission theory in organic molecular crystals.<sup>4,11–14</sup> Those early theoretical works were focused in the development of kinetic models for singlet exciton fission. These theories were mostly motivated by experimental measurements of external magnetic field effects on fluorescent emission.<sup>15</sup> The singlet fission kinetic models

developed in the late 1960's and 1970's mostly rely on the singlet fission and triplet–triplet annihilation model developed by Johnson and Merrifield,<sup>10,16</sup> later improved by Suna,<sup>17</sup> who included the effects of triplet exciton diffusion in the model. These theories were very successful, reproducing experimental observations in molecular crystals, although the limitations of quantum chemistry electronic structure calculations at that time prevented the detailed description of the electronic states involved in the singlet fission mechanism. Experimental efforts delivered more details of singlet fission in anthracene and tetracene crystals,<sup>18,19</sup> while attempts to observe singlet fission in naphthalene and pyrene crystals did not succeed.<sup>12</sup> In the following years, the research community paid less attention to the phenomenon and the most relevant advances in the field were related to the observation of exciton fission in carotenoids<sup>20</sup> and conjugated polymers.<sup>21,22</sup>

It is widely accepted that the interest for the singlet fission process was strongly revitalized in 2006, when Hanna and Nozik suggested multiple exciton generation (MEG) in organic materials through singlet exciton fission as a path to overcome the thermodynamic upper limit for power conversion efficiency in single-junction solar cells (~33%)<sup>23</sup> (i.e., the Shockley–Queisser limit),<sup>24</sup> linking the research on singlet fission to its potential use in photovoltaics. The works of Michl and co-workers have played a crucial role in the development of the modern theory of singlet fission, and they have strongly inspired the research in the field. Michl et al. established the requirements for a good singlet fission sensitizer and provided a recipe for the computational search of organic chromophores to be used in solar cells.<sup>25,26</sup> In 2010, Smith and Michl published a thorough review on the theory and experimental progress in singlet fission,<sup>2</sup> updated in 2013 by the same authors,<sup>3</sup> which have been cited in virtually all the subsequent investigations in singlet fission. The present review discusses the main advances up to 2017 regarding the theoretical aspects of the singlet fission process and its computational modeling.

### 1.2. Experimental Measurements

Experimentally, singlet fission has been detected and characterized by a variety of measurements, such as delayed fluorescence, via magnetic variations of spectroscopic features, or using photoinduced transient absorption techniques. Fluorescent emission occurring on a time scale much longer than the singlet radiative lifetime (delayed fluorescence) is a signature of the recombination of two triplet excitons,<sup>27</sup> and it has been used many times as indirect detection and characterization of singlet exciton fission.<sup>28–33</sup> Other approaches, such transient absorption or time-resolved two-photon photoemission spectroscopies, try to detect triplets directly. Transient absorption measures the radiation transmission variation of a material in response to photoexcitation. The appearance of laser sources able to launch pulses with femtosecond duration has provided the opportunity to employ transient absorption spectroscopy to investigate the time-evolution of electronic states in singlet fission, which has become one of the main experimental techniques to detect singlet fission and study its dynamics. Theoretical rationalization of excited state absorption measurements applied to the study of singlet fission in solid pentacene has been discussed in detail by Khan and Mazumdar.<sup>34</sup> Detection of singlet fission has also been done through spectroscopic dependence with applied magnetic field. In particular, analysis of the variations on the photocurrent with the external

magnetic field has been used in numerous occasions to study photovoltaic devices incorporating a singlet fission component.<sup>35–38</sup> Detailed discussion of these characterization techniques can be found somewhere else, while reviews of their application to the study of singlet fission has been done already<sup>39–42</sup> and is out of the scope of the present work.

### 1.3. Application in Solar Cells

Since the suggestion by Hanna and Nozik,<sup>23</sup> the main long-term goal of the research on singlet fission has been its potential use in solar cells, either to convert solar photons into electricity in photovoltaic devices or to produce solar fuels. The promising potential of the integration of singlet fission materials in solar cell architectures is to mitigate the energy losses due to the conversion of the excess kinetic energy of hot carriers to heat by generating a second exciton for those solar photons with energies at least twice the band gap of the semiconductor.<sup>43</sup>

Importantly, in order to surpass the Shockley-Queisser limit, singlet fission solar cells require two or more light harvesting components: a singlet fission material capable of absorbing high-energy photons and a chromophore responsible for converting lower energy solar radiation into a single electron–hole pair per solar photon.<sup>23,44</sup> Theoretically, the use of singlet fission in photovoltaics can double the induced photocurrent for short wavelength photons with the voltage of a single junction cell. One of the potential loss mechanisms in singlet fission solar cells is the electron transfer channel from the  $S_1$  state (i.e., prior to the multiexciton formation). Hence, in order to generate two charge carriers per absorbed photon, singlet fission needs to be fast.<sup>45</sup> So far, solar cells incorporating singlet fission materials have achieved external quantum efficiencies of up to 126% and internal quantum efficiencies close to 200%.<sup>35,46</sup> Advances in the use of singlet fission materials in third generation photovoltaic technologies<sup>47</sup> have been recently discussed by Xia and co-workers.<sup>48</sup>

Integration of singlet fission materials in solar cell devices can be done by charge separation of triplet excitons combining a singlet fission donor and an acceptor. The ionization of triplets at the donor–acceptor interface was demonstrated for the first time by Rao et al. using pentacene and  $C_{60}$  as the singlet fission compound and electron acceptor, respectively.<sup>49</sup> The list of requirements at the pentacene– $C_{60}$  interface needed to increase solar cell efficiencies has been theoretically evaluated by Aryanpour and collaborators.<sup>50</sup> Since then, several other heterojunctions have been proposed and investigated in order to improve charge generation.<sup>35,37,46,51–54</sup>

Alternatively, singlet fission compounds can be potentially used as sensitizers coupled to typical semiconductor solar cells such crystalline or amorphous silicon<sup>55</sup> or in perovskites.<sup>56</sup> The theoretically predicted efficiency for a singlet fission sensitized parallel tandem solar cell is ~45%.<sup>55</sup> Compared to inorganic semiconductors, organic systems present rather poor charge transport properties, limiting their use in photovoltaics. A possible strategy to circumvent such limitation could be the use of singlet fission molecular sensitizers in dye-sensitized solar cells (DSSCs).<sup>57</sup> The integration of singlet fission in a DSSC was already proposed in 2006<sup>25</sup> and has been successfully tested using 1,3-diphenylisobenzofuran as the singlet fission sensitizer chemically linked through a carboxylic acid group to mesoporous  $TiO_2$ .<sup>58</sup> Competition between electron injection to the  $TiO_2$  conduction band from  $T_1$  and  $S_1$ , which sensibly affects the short circuit photocurrent, can be modulated by the

use of a spacer layer between the dye and the semiconductor or by chemical design of the singlet fission sensitizer to reduce injection from the excited singlet. Moreover, it has been suggested that the spacer layer could be also used to optimize the aggregation morphology of the singlet fission sensitizers on the surface.<sup>59</sup>

## 2. OVERVIEW OF THE SINGLET FISSION PROCESS

### 2.1. Fundamental Aspects

Singlet fission, also referred to as singlet exciton fission, is a photophysical reaction in which a spin singlet excited state is converted to two spin triplet excitons (eq 1). Although it connects the singlet and triplet manifolds, singlet fission is a spin-allowed process since the two generated triplets are coupled as an overall singlet. Conservation of spin symmetry allows for a fast reaction (i.e., on time scales of the order of a few picoseconds or even subpicosecond).



The singlet fission phenomenon is a downconversion process of high-frequency photons into lower-energy excitons and was initially defined as the reverse of the triplet–triplet annihilation reaction.<sup>1,9</sup> Singlet fission can be also seen as the molecular analogue to MEG in inorganic semiconductors, such in quantum dots,<sup>60</sup> sometimes also termed impact ionization,<sup>61</sup> and quantum cutting in lanthanide ions.<sup>62–64</sup> Although the formation of multiple excitons is similarly very fast in both singlet fission and MEG, they present important fundamental differences. While the singlet fission process results in two triplet excitons located in two monomers, in MEG, the excitons are created in a single nanocrystal or quantum dot. One of the advantages of singlet fission is the fact that triplet excitons in organic materials live for microseconds, while excitons in inorganic nanostructures tend to rapidly decay via Auger recombination, typically in a few tens of picoseconds,<sup>65</sup> effectively erasing electron–hole pairs produced via MEG. Comparison between MEG in semiconductor nanocrystals and singlet fission in organic molecules regarding their potential use to boost the efficiency of solar cells in photovoltaics and the production of solar fuels has been discussed in great detail by Beard et al.<sup>66</sup>

Often, the singlet fission process is described as the result of two consecutive steps where the initial excited state is assumed to be related to the lowest excited singlet of a monomeric chromophore (eq 2).



Since the singlet fission photophysical reaction begins from an excited singlet state, it requires of an initial activation energy acting as the singlet fission driving force. This activation energy is typically obtained through photoabsorption and initial electronic promotion of the system to an optically active state, although, in principle, singlet fission could take place using other activation sources.<sup>67</sup> Photoexcitation of the system triggers the (coherent or incoherent) formation of an intermediated state, the singlet fission  $^1TT$  precursor, with a very particular electronic structure containing the seed for the formation of two triplet states. Once the intermediate state is formed it can, in principle, dissociate in two independent triplets via the Dexter energy transfer mechanism.<sup>68</sup> Electronic coupling between the two triplet excitons is lost upon spatial separation, but the two triplets might remain entangled as an

overall spin singlet (quantum or spin coherence).<sup>69,70</sup> Experimentally, it has been shown that spin coherence can be preserved for quite a long time, typically in the order of nanoseconds.<sup>71,72</sup> Theoretical investigations in singlet fission have focused their attention to address static and dynamic aspects of the photophysical reaction up to the formation of two (electronically) independent triplets, while other important closely related processes like the description of singlet and triplet state diffusion in singlet fission materials and, in particular, the loss of spin coherence between the fission triplets as they diffuse through the electronic material remain largely unexplored.

## 2.2. Requirements for Efficient Singlet Fission

In spite of numerous efforts, the amount of organic materials able to undergo singlet fission has remained fairly limited due to the restrictive list of requirements necessary for a compound to be able to exhibit such phenomenon. The properties for a good singlet fission sensitizer were nicely established by Michl et al.,<sup>25,26</sup> and they have been repeatedly mentioned and discussed in the literature.

**Thermodynamic Condition.** Spontaneous singlet fission reaction requires the energy of  $S_1$  to be equal to or higher than twice the energy of the lowest triplet:  $E(S_1) \geq 2E(T_1)$ . Relative energies should be evaluated at the minima of the potential energy surfaces (PES) of  $S_1$  and  $T_1$  states since the fission rate is slower than the vibration relaxation rate. Taking into consideration state specific relaxation effects might be crucial in order to predict the right energetics and/or trends within a family of systems, due to the fact that differences on the geometry relaxation of the lowest singlet and triplet can be substantial.<sup>33</sup> Moreover, enthalpy and entropy contributions from the nuclei degrees of freedom to the Gibbs free energies should be taken into account. Instead, the use of the computed vertical energy to the bright state at the Franck–Condon geometry would correspond to the case where singlet fission occurs with no energy loss from the initial photoexcitation.

**Kinetic Condition.** It is well-known that a too exoergic process is detrimental for singlet fission, since it slows down the rate of the photophysical reaction. Besides, it would result in an energy loss through heating of the system. Therefore, it seems that optimal energetic conditions are found for those systems with  $S_1$  level slightly above twice the  $T_1$  energy, like in the case of pentacene.

**Deactivation Channels.** In order for singlet fission to be efficient it must outcompete alternative decay paths, which gives rise to additional energetic requirements. One of the potential interfering channels to singlet fission is the recombination of the fission triplets into higher spin states, that is the triplet (eq 3) and quintet (eq 4) manifolds, which would hinder the generation of two electron/hole pairs.

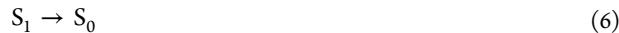


Triplet–triplet fusion to the triplet manifold is energetically forbidden if the second triplet lies higher in energy than the two lowest triplets:  $E(T_2) > 2E(T_1)$ , which is commonly referred as the second singlet fission condition. The lowest quintet state in organic molecules is typically rather high in energy, and the  $E(Q_1) > 2E(T_1)$  condition related to the photophysical reaction in eq 4 is easily achieved. These two conditions can be related to the tetraradicaloid character of the chromophore being unfavorable for singlet fission (see section 7.2).

Another potential competing pathway is the direct transition from the excited singlet into the triplet manifold through intersystem crossing (ISC) (eq 5). In general, this channel is not considered in the frame of singlet fission, since the typical organic conjugated molecules exhibiting good fission properties hold weak spin–orbit couplings, resulting in inefficient ISC. On the other hand, the recent investigations in the search of novel singlet fission sensitizers through the introduction of heavy heteroatoms might change this situation facilitating the ISC path through the heavy atom effect.<sup>73</sup>



Photoexcited flexible molecules are prompt to efficiently decay back to the ground state (eq 6) through symmetry allowed interstate crossings (conical intersections).<sup>74–76</sup> Polyenes, such as the retinal molecule, are good examples of internal conversion to  $S_0$  through molecular relaxation along the  $S_1$  PES.<sup>77–80</sup> Therefore, in the design of molecular candidates for singlet fission, it is advisable to avoid floppy structures. In fact, the flagship singlet fission molecules, tetracene and pentacene, as well as other good singlet fission compounds present rather rigid molecular geometries.



The simultaneous coexistence of two (or more) spatially close singlet excitons in large exciton densities, which can be generated by intense radiation and for long-lived  $S_1$  states, can favor the singlet–singlet annihilation channel (eq 7), reducing the number of fission events.<sup>81</sup>



Other unwanted deactivation paths potentially competing against singlet fission are the recombination to the single-exciton manifold, which can be circumvented with long triplet-pair lifetimes to allow for triplet–triplet separation, the formation of charge-separated states, or the decay to dark singlet states.<sup>82</sup>

**Comparison to Experiment.** The relative energy requirements for the  $S_1$ ,  $T_1$ ,  $T_2$ , and  $Q_1$  states are typically computationally evaluated at the molecular level, although matrix effects can sensibly modify the relative energies of the low-lying states, even switching their energetic order or transforming their electronic nature. Hence, although the molecular approach has been demonstrated to be a good and efficient first step for the screening of singlet fission compounds, it is important to keep in mind that final energies in singlet fission materials might be notably affected by the environment. Comparison of molecular energies to experimental values has to be done with precaution. In addition to the intrinsic errors of any chemistry model, which might be system-dependent, much attention has to be paid when comparing these computed energies to experimental values, since these might strongly depend on experimental conditions. For these reasons, if possible, it might be advisable to benchmark molecular energies obtained with feasible methods for the exploration of large sets of chromophores to high-level calculations (i.e., controlled conditions).

**Other Requirements.** In addition to the above conditions, other properties might be necessary for practical consideration. In order for singlet fission compounds to be efficiently used as solar cell sensitizers, good light-harvesting properties are desirable (i.e., large absorption coefficients), which can be achieved with  $\pi$ -conjugated rigid chromophores. Also, molecular

candidates should be chemically photostable for a long period of time. In fact, chemical instability is one of the main issues for the potential application of long linear polyacenes, which present poor stabilities due to their increasing diradical character with the molecular length. Pristine acenes have been experimentally obtained up to six fused rings (hexacene),<sup>83</sup> and only the use of stabilizing strategies based on chemical substitution has allowed the successful synthesis of stable acenes up to nonacene (nine benzene rings).<sup>84</sup> In this sense, emergent singlet fission chromophores with long-term stabilities and strong light absorbing capabilities, such as perylenediimide<sup>85,86</sup> and terrylenediimide derivatives<sup>87–89</sup> or diketopyrrolopyrroles,<sup>90,91</sup> might soon become potential alternatives in real applications.

The tendency of acenes to react with fullerenes through the Diels–Alder reaction<sup>92,93</sup> constitutes a clear example of their chemical instability resulting in a practical impediment for the design of singlet fission solar cells based on donor–acceptor heterojunctions. Another limiting factor of the acene–fullerene system is the presence of higher acceptor levels in C<sub>60</sub>, which might favor the one-electron transfer from the donor, hindering the injection of two electrons per harvested photon.<sup>94</sup> In order to surpass such chemical instability and efficiency losing issues, alternative acceptors have been proposed to replace fullerenes.<sup>95–100</sup>

### 3. ELECTRONIC STATES INVOLVED IN SINGLET FISSION

The mechanistic study of singlet fission requires the detailed description of the electronic states directly and indirectly involved in the process. The complexity of the singlet fission phenomenon and the different nature of the electronic states potentially involved represent a real challenge for any given excited state method. To that end, a plethora of electronic structure approaches and molecular models have been applied to undercover the intricacies of the singlet exciton fission, the nature of the electronic states, and the interstate properties.

Since the final product of the photophysical fission reaction corresponds to two independent triplets, singlet fission can take place in systems containing at least two chromophoric moieties. Generally speaking, the computational characterization of low-lying electronic states in multichromophore systems can be approached following diabatic or adiabatic methodologies, both with their advantages and drawbacks. The large majority of quantum chemistry models are based on the adiabatic picture and standard quantum chemistry codes typically work within the adiabatic basis. On the other hand, the use of diabatic states is preferred when exploring the time evolution of electronic states. Although detailed reviews on the foundations and properties of these two representations can be found somewhere else,<sup>101,102</sup> in the following, I briefly revisit the most relevant aspects of the two representations with direct connection to the computational modeling of singlet fission.

#### 3.1. Adiabatic and Diabatic Representations

The electronic structure for a molecular system can be obtained by solving the time-independent (nonrelativistic) Schrödinger's equation:

$$H(\mathbf{r}, \mathbf{R})|\Phi(\mathbf{r}, \mathbf{R})\rangle = E|\Phi(\mathbf{r}, \mathbf{R})\rangle \quad (8)$$

where  $\mathbf{r}$  and  $\mathbf{R}$  are the positions of electrons and nuclei respectively,  $\Phi(\mathbf{r}, \mathbf{R})$  is the total wave function, and  $H(\mathbf{r}, \mathbf{R})$  is the full Hamiltonian. The Hamiltonian is commonly expressed

as the contribution of nuclear kinetic energy  $T_N(\mathbf{R})$  and the electronic Hamiltonian  $H_{el}(\mathbf{r}; \mathbf{R})$ , which depends parametrically on the nuclear coordinates (eq 9).

$$H(\mathbf{r}, \mathbf{R}) = T_N(\mathbf{R}) + H_{el}(\mathbf{r}; \mathbf{R}) \quad (9)$$

Diagonalization of the electronic Hamiltonian yields to the adiabatic basis of eigenstates  $\{\Psi_I\}$  (eq 10), which are typically approximated by electronic structure quantum chemistry models under the Born–Oppenheimer approximation.

$$H_{el}(\mathbf{r}; \mathbf{R})|\Psi_I(\mathbf{r}; \mathbf{R})\rangle = E_I(\mathbf{R})|\Psi_I(\mathbf{r}; \mathbf{R})\rangle \quad (10)$$

Since the set of adiabatic states forms a complete basis for the Hilbert space, the total wave function can be expressed as a linear combination of  $\{\Psi_I\}$ ,

$$\Phi(\mathbf{r}, \mathbf{R}) = \sum_I \Theta_I(\mathbf{R})\Psi_I(\mathbf{r}; \mathbf{R}) \quad (11)$$

where  $\{\Theta_I\}$  represents the nuclear wave functions. Alternatively, the nuclear-electron wave function can be expanded by a complete set of electronic states not depending on the nuclei coordinates (i.e., diabatic basis  $\{\Xi_I\}$ )

$$\Phi(\mathbf{r}, \mathbf{R}) = \sum_I \Theta'_I(\mathbf{R})\Xi_I(\mathbf{r}) \quad (12)$$

Diabatic states do not diagonalize the electronic Hamiltonian and can be seen as states with well-defined electronic structure character that do not change upon distortions of the nuclear structure.

The time evolution of electronic excited states in molecular systems define and shape their photophysical and photochemical properties, such as the singlet fission process, and can be described by the time-dependent Schrödinger's equation of  $\Phi$ .

$$i\hbar \frac{\partial}{\partial t} |\Phi(\mathbf{r}, \mathbf{R})\rangle = H(\mathbf{r}, \mathbf{R})|\Phi(\mathbf{r}, \mathbf{R})\rangle \quad (13)$$

If we develop the total wave function in eq 13 by the adiabatic expansion (eq 11), we arrive at an equation describing the time-evolution of nuclear wave functions on different interacting adiabatic states:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Theta_I(\mathbf{R}) &= \left( \sum_{\alpha} \frac{-\hbar^2 \nabla_{\alpha}^2}{2m_{\alpha}} + E_I(\mathbf{R}) \right) \Theta_I(\mathbf{R}) \\ &\quad - \sum_{J\alpha} \frac{\hbar^2}{2m_{\alpha}} (\langle \Psi_I(\mathbf{R}) | \nabla_{\alpha}^2 | \Psi_J(\mathbf{R}) \rangle \\ &\quad + 2 \langle \Psi_I(\mathbf{R}) | \vec{\nabla}_{\alpha} | \Psi_J(\mathbf{R}) \rangle \cdot \vec{\nabla}_{\alpha}) \Theta_J(\mathbf{R}) \end{aligned} \quad (14)$$

where  $\alpha$  index runs over all nuclear coordinates and  $m_{\alpha}$  are the associated masses. The last two terms on the right-hand side of eq 14, neglected in the Born–Oppenheimer approximation, are the first- and second-derivative couplings responsible for the mixing between the (adiabatic) electronic PESs. On the other hand, if we use the diabatic electronic states instead, all the derivative coupling terms vanish, and we arrive at eq 15, where the diabats are coupled through the electronic Hamiltonian. Hence, off-diagonal matrix elements of the electronic Hamiltonian in the diabatic bases are called diabatic or electronic couplings.

$$i\hbar \frac{\partial}{\partial t} \Theta'_I(\mathbf{R}) = - \left( \sum_a \frac{\hbar^2 \nabla_a^2}{2m_a} + \sum_J \langle \Xi_I(\mathbf{R}) | H_{el} | \Xi_J(\mathbf{R}) \rangle \right) \Theta'_I(\mathbf{R}) \quad (15)$$

Eqs 14 and 15 highlight the importance of interstate couplings to study the dynamics of photophysical and photochemical processes, where several PESs might be involved, as in singlet fission. Computation of electronic and derivative couplings within the framework of singlet fission will be discussed in sections 5.1 and 5.2, respectively.

Since the diabatic basis proportionates a clear physical picture of the fission process and has a closer relationship to the state characterization employed in experimental investigations to label initial, intermediate, or virtual and final states in singlet fission, the diabatic picture has been predominant in the field. On the other hand, the adiabatic states are “natural” solutions of the electronic Hamiltonian. As a result, many theoretical studies relying on the computation of adiabatic electronic states through the diagonalization of an ab initio Hamiltonian make use of diabatization schemes either to translate the results to the diabatic language or to circumvent the calculation of derivative couplings. Several examples of the use of diabatization procedures based on the rotation of the computed adiabatic eigenstates into a quasi-diabatic basis of local states (eq 16) can be found somewhere else.<sup>103–105</sup>

$$|\Xi_I(\mathbf{r})\rangle = \sum_J U_{JI}(\mathbf{R}) |\Psi_I(\mathbf{r}; \mathbf{R})\rangle \quad (16)$$

Although formally the adiabatic and diabatic perspectives are equally valid, important differences may arise upon the approximations defining the electronic structure methodology chosen to obtain adiabatic or diabatic states, their energies, and couplings. The adequacy of the use of the diabatic and adiabatic representations in the frame of the singlet fission process is of vital importance and has been discussed by several authors.<sup>106–108</sup> In particular, the suitability of the diabatic approach for the treatment of singlet fission has been seriously questioned.<sup>106</sup> The practical limitation of electronic structure calculations of singlet fission based on diabatic states is related to the intrinsic difficulty to obtain proper diabatic (or quasidiabatic) states,<sup>109</sup> rather to an intrinsic deficiency of the diabatic approach per se. In particular, the use of a few (model) diabatic states based on single configurations build as distinct electronic occupancies of the sensitizer’s frozen frontier orbitals; although it can be very useful to obtain physical insight and qualitative understanding of the singlet fission mechanism, it might be unable to capture the complexity of the fission process and the subtleties of the states involved. One has to be cautious when pursuing a quantitative description from such models. Moreover, different approximations to the definition of diabats might result in sensible quantitative discrepancies or even drive to qualitative differences and apparent contradictions regarding the character of the electronic states or the magnitude of the computed couplings. This point can be sometimes a source of confusion between apparently similar methodologies. A prominent example of this situation relates to the nature of the optically active state. The simple idea of an initial photoexcited state with pure diabatic character corresponding to a localized exciton (or a combination of them, i.e., Frenkel exciton) might not be appropriate in many singlet fission materials, since electrons in interacting chromophores, such as in  $\pi$ -conjugated molecular

crystals, might be strongly correlated. Hence, diabatic models formally treating the singlet fission mechanism in terms of single electron hops between weakly interacting chromophores can drive an inaccurate description of the phenomenon.<sup>110,111</sup>

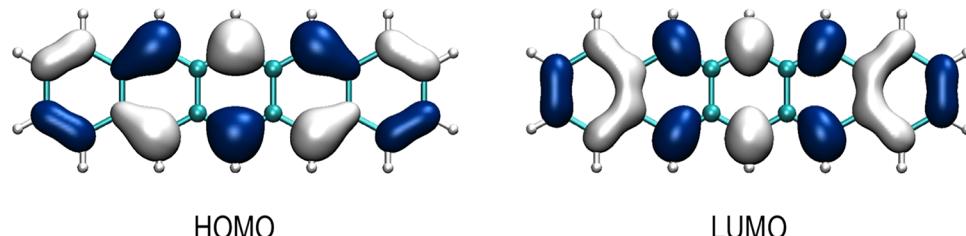
All in all, while the diabatic approach provides a picture of the singlet fission process in terms of states with well-defined electronic character, facilitating the identification of fission mechanisms, assumptions of what are the important electronic configurations responsible for the photophysics of the system might result in important errors. In other words, the potential unsuitability of diabatic approximations to treat the singlet fission mechanism relies on the size and flexibility of the basis of diabatic states chosen. On the other hand, the adiabatic approach is free of such conjectures, and the nature of electronic states emerges naturally by solving the excited states model equations (with no need for prepared contributions). In particular, calculations in terms of adiabatic states can identify unanticipated electronic contributions [e.g., doubly excited (dark) states], which can be completely omitted when using a predefined basis of diabatic states. The practical limitations of the adiabatic approach reside on the reliability of the chosen electronic structure method (e.g., energy functional or atomic basis set) (notice that these limitations are also present in any diabatic model). Moreover, the main features regarding the character of electronic states can be also recovered a posteriori by deconvoluting adiabatic states through diabatization techniques or by decomposition of the excited state wave functions. For these reasons, if possible, it is advisable to complement or validate diabatic state calculations with adiabatic methods in order to obtain a more robust computational analysis of singlet fission.

### 3.2. Electronic States

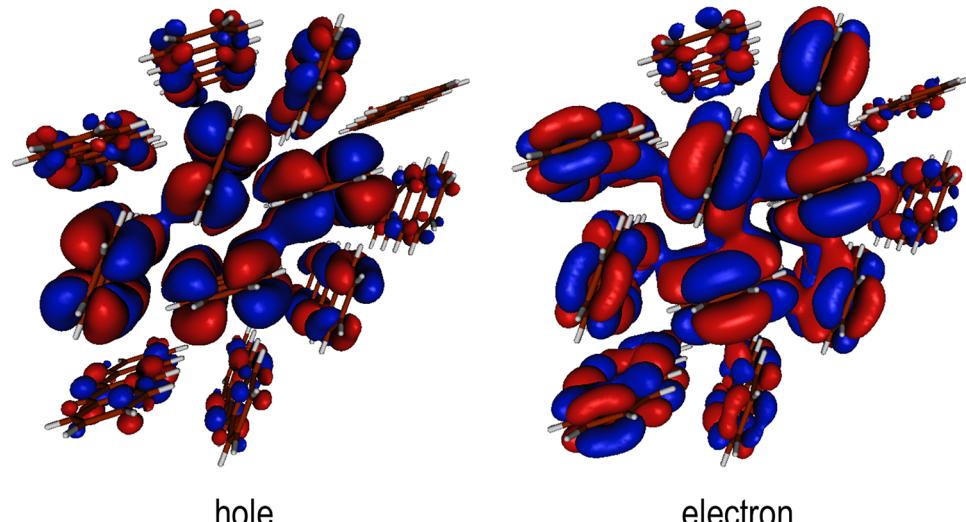
The main electronic states in singlet fission are the ones describing the photophysical reaction in eq 2, that is the lowest spin-singlet with monoexcitonic character ( $S_1$ ), the two independent triplet states ( $T_1$ ), and the multiexcitonic ( ${}^1\text{TT}$ ) state. Moreover, other states might be involved in the overall process, in particular the potential participation of charge transfer (CT) and/or charge resonant (CR) states has been largely discussed in the singlet fission literature.<sup>111</sup> In the following, I present a short description of these and other electronic low-lying excited states highlighting the most significant properties regarding to their role in singlet fission.

**3.2.1. Singlet Exciton.** Initial photoexcitation promotes the singlet fission system to an optical spin singlet state that, by means of the transition dipole approximation, it is expected to correspond to a single electron transition (at least partially). In the case of weakly interacting chromophores, the optical excitation can be related to a molecular bright state. This relation is exact in the limit case of singlet fission in dilute solution.<sup>112</sup> The nature of the molecular bright and other low-lying singlet states and their relative energetic order has been discussed in the frame of singlet fission in terms of different chromophore classes.<sup>2</sup> In singlet fission, it is commonly assumed that if the optical state is not the lowest excited singlet ( $S_1$ ), the system rapidly decays to  $S_1$  (Kasha’s rule<sup>113</sup>) before it undergoes fission, although the possibility of singlet fission from upper vibrational states of  $S_1$  or from a higher excited singlet ( $S_n$ )<sup>114</sup> have also been considered as viable routes to overcome endoenergicity.

In the singlet fission literature, the lowest single-electron excited singlet of the overall system commonly takes the



**Figure 1.** Isodensity representation of the HOMO (left) and LUMO (right) for the pentacene molecule.



**Figure 2.** Natural transition orbitals<sup>141</sup> for  $S_1$  in tetracene representing the exciton delocalization. Hole (left) and electron (right) isodensities have been computed for a cluster of 12 tetracene molecules in the crystal structure.

labeling from the lowest excited state in the molecule or monomer ( $S_1$ ), but it has also been identified using the condensed matter physics terminology as local exciton (LE), Frenkel exciton (FE), or simply exciton state (EX). In this review, I use  $S_1$  to generically label the excited singlet state that in dimers, aggregates, or extended systems can be related to the lowest excited singlet state of the monomer (molecule or fragment), and I will employ the LE (or FE) terminology to describe the character of the exciton.

In some cases, in particular when the molecular sensitizer exhibits some diradical character, the lowest singlet excited state could have multiexcitonic character, like for all-*trans* polyenes longer than butadiene.<sup>116,117</sup> In fact, it has been argued that the doubly excited dark state (D) in the pentacene molecule might be directly involved in the singlet fission mechanism since computed energies suggested that this dark state lies energetically below the one-electron optical transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Figure 1).<sup>118</sup> But, experimental measurements<sup>119,120</sup> and very accurate high-level calculations<sup>121</sup> have located the molecular D state above  $S_1$ , which seems to definitely rule out the involvement of the molecular doubly excited state in the exciton fission mechanism, at least in pentacene.

The general photophysical reaction defining singlet fission (eq 1), might suggest that the fission mechanism involves the energy repackaging of a singlet exciton localized on one molecule (or molecular fragment) into two triplets on two different chromophores. Although this picture is recursively used in the literature,<sup>2,3</sup> this model does not seem to represent the physical nature of the excitonic state ( $S_1$ ) in extended

systems such as organic molecular crystals or aggregates, since singlet excitons have a strong tendency to delocalize over several chromophores.<sup>11,122–124</sup> Computational evaluation of exciton delocalization in crystalline pentacene<sup>125</sup> by means of the Green's function method (GW)<sup>126–129</sup> and the Bethe-Salpeter equation (BSE)<sup>130–134</sup> calculations show an average electron–hole distance greater than 6 Å, while computations on molecular clusters of tetracene (Figure 2), 5,12-diphenyltetracene, and rubrene estimate that, in the crystal, at least seven molecules participate to the photoexcited state,<sup>135</sup> in line with time-resolved spectroscopy measurements on anthracene<sup>136</sup> and tetracene,<sup>137</sup> suggesting exciton delocalization over ten molecules. Moreover, it has been seen that the extent of electron and hole delocalization in tetracene and pentacene varies with intermolecular vibrations,<sup>138</sup> which might have an important impact on the transition to the multiexcitonic state (first step in eq 2) by controlling the  $S_1 \rightarrow {}^1\text{TT}$  nonadiabatic coupling. Experimental measurements in nanocrystals of pentacene derivatives have suggested that indeed exciton delocalization increases the fission efficiency due to fast formation of the triplet-pair state.<sup>139</sup> In the same direction, detection of vibrational coherent transfer between photoexcited singlet and singlet fission triplets in TIPS-pentacene suggests that delocalization of  $S_1$  allows for ultrafast singlet exciton fission.<sup>140</sup>

**3.2.2. Triplet State.** The final product state of singlet fission (i.e., the independent triplet) has a strong molecular character (even in extended systems) and, to a first approximation, corresponds to the single-electron occupation of the HOMO and LUMO of the chromophore. The rather large exchange interaction in many organic conjugated

molecules<sup>142,143</sup> results in significant singlet-triplet energy separation, which can be on the order of 1 eV.<sup>123</sup> Within a two-electron model, the singlet–triplet energy gap can be approximated as twice the exchange integral between the HOMO and LUMO ( $K_{hl}$  in eq 17).<sup>144</sup> The sizable energy difference between the lowest excited singlet and triplet states allows for the possibility of organic materials to undergo single fission, which is not possible in inorganic systems such as quantum dots, where singlets and triplets are virtually degenerate and multiexciton generation follows a different mechanism.<sup>66,145–147</sup>

$$E(S_1) - E(T_1) \approx 2K_{hl} \quad (17)$$

Moreover, due to the lack of electron–hole (repulsive) exchange interaction, triplet excitons exhibit larger binding energies and are more localized than singlet excitons.<sup>148</sup> This behavior results in very similar vertical transition energies to  $T_1$  measured in the solid phase and in solution (or in gas phase) compared to the important redshift typically observed for the  $S_1$  excitation energies,<sup>149</sup> although this might not always be the case, as it has been suggested that the triplet exciton of perylenediimide (PDI) is notably stabilized in the solid state (about 0.14 eV while  $S_1$  redshifts 0.26 eV).<sup>150</sup>

**3.2.3. Triplet-Pair State.** The fission process from the lowest single exciton ( $S_1$ ) to two independent triplet states ( $T_1$ ) occurs through an intermediate state with multiexciton character that corresponds to a triplet-pair coherently coupled as an overall spin singlet, which in terms of valence bond theory can be described as a strong spin correlation.<sup>151</sup> This state is a cornerstone in the singlet fission mechanism, since it provides a spin-allowed pathway between the excited singlet and triplet manifolds. Within the singlet fission literature the correlated triplet-pair state is typically labeled as  $^1\text{TT}$  (or  $^1\text{T}_1\text{T}_1$ ), but other denominations are also used such as multiexciton state (ME), dark state (D),<sup>33</sup> or doubly excited state ( $^1\text{D}^{**}$ ).<sup>152</sup> In this review, I use the  $^1\text{TT}$  label, since it is the most common nomenclature in the field and provides a more detailed description of the electronic structure nature of the state (e.g., differentiating with respect to other multiexciton states). However, it is important to stress that although I chose to use a label corresponding to a well-defined electronic structure (diabatic state), the multiexciton intermediate can mix to other electronic configurations and can be described as a pure  $^1\text{TT}$  only asymptotically. Contributions from other diabatic states to the overall adiabatic wave function have been evaluated to account for ~10% in typical organic crystals.<sup>106</sup>

The electronic structure nature of the  $^1\text{TT}$  state poses a real challenge from a theoretical and computational point of view. Moreover, experimental detection and characterization of the triplet-pair state faces more difficulties than for other excited states like  $S_1$ ,  $T_1$ , or CT states and has been directly observed on a few occasions.<sup>112,153,154</sup> On the basis of (orthonormal) molecular orbitals, the spin complete form of the triplet-pair state within the dimer model is built as a linear combination of couplings between two monomeric triplet states with each sum of the two local spin quantum numbers ( $m_s$ ) equal to zero (eq 18),

$$|^1\text{TT}\rangle = \frac{1}{\sqrt{3}}(|T_+T_-\rangle + |T_-T_+\rangle - |T_0T_0\rangle) \quad (18)$$

where  $T_+$ ,  $T_-$ , and  $T_0$  correspond to the three  $m_s$  triplet microstates of the monomer. Eq 18 can be developed as six

doubly excited configurations by expanding the direct product of monomeric triplets (Figure 3).

$$|^1\text{TT}\rangle = \frac{1}{\sqrt{3}} \left[ \begin{array}{c} \uparrow \downarrow \\ \downarrow \uparrow \end{array} \right]_+ \left[ \begin{array}{c} \downarrow \uparrow \\ \uparrow \downarrow \end{array} \right]_+ \frac{1}{2} \left[ \begin{array}{c} \downarrow \uparrow & \uparrow \downarrow & \downarrow \uparrow & \uparrow \downarrow \\ \uparrow \downarrow & \downarrow \uparrow & \uparrow \downarrow & \downarrow \uparrow \end{array} \right]_+ \left[ \begin{array}{c} \uparrow \downarrow \\ \downarrow \uparrow \end{array} \right]_+ \quad (19)$$

Figure 3. Electronic configurations for the  $^1\text{TT}$  state in terms of HOMO and LUMO (bottom and top) for two monomers (left and right) in a dimer model.

Alternatively, the  $^1\text{TT}$  state can be expressed in terms of the zero-field triplet spin states  $|x\rangle$ ,  $|y\rangle$ , and  $|z\rangle$ :<sup>155</sup>

$$|^1\text{TT}\rangle = \frac{1}{\sqrt{3}}(|xx\rangle + |yy\rangle + |zz\rangle) \quad (19)$$

The two (local) triplets might also couple into an overall triplet or quintet state. The expressions for the triplet and quintet triplet-pair states are shown in eqs 20–24, where super indices indicate spin multiplicity and  $m_s$  values, respectively.

$$|^3,0\text{TT}\rangle = \frac{1}{\sqrt{2}}(|T_+T_-\rangle - |T_-T_+\rangle) \quad (20)$$

$$\begin{aligned} &|^3,+1\text{TT}\rangle = \frac{1}{\sqrt{2}}(|T_+T_0\rangle - |T_0T_+\rangle); \\ &|^3,-1\text{TT}\rangle = \frac{1}{\sqrt{2}}(|T_-T_0\rangle - |T_0T_-\rangle) \end{aligned} \quad (21)$$

$$|^5,0\text{TT}\rangle = \frac{1}{\sqrt{6}}(|T_+T_-\rangle + |T_-T_+\rangle + 2|T_0T_0\rangle) \quad (22)$$

$$\begin{aligned} &|^5,+1\text{TT}\rangle = \frac{1}{\sqrt{2}}(|T_+T_0\rangle + |T_0T_+\rangle); \\ &|^5,-1\text{TT}\rangle = \frac{1}{\sqrt{2}}(|T_-T_0\rangle + |T_0T_-\rangle) \end{aligned} \quad (23)$$

$$|^5,+2\text{TT}\rangle = |T_+T_+\rangle; \quad |^5,-2\text{TT}\rangle = |T_-T_-\rangle \quad (24)$$

The electronic interaction between the two triplets at short distances in the singlet state is stronger than for the  $^3\text{TT}$  and  $^5\text{TT}$  counterparts, and this additional stabilizing energy has been related to the energy required to dissociate the two triplets.<sup>156</sup> The singlet triplet-pair state can be stabilized by configuration interaction to other singlet configurations, while the quintet state preserves a much larger pure diabatic character. The mixing of  $^5\text{TT}$  to other quintets is limited because these states are generally much higher in energy.<sup>157</sup> Hence, the binding energy of the two triplets can be approximated as

$$E_b \approx E(^5\text{TT}) - E(^1\text{TT}) \quad (25)$$

The role of the  $^5\text{TT}$  as an intermediate state in singlet fission has been hypothesized by means of the spin Hamiltonian of interacting triplets.<sup>158,159</sup> The formation of a triplet-pair quintet state from the spin pure  $^1\text{TT}$  can be understood by the action of spin dipole–dipole interactions between the two triplets,<sup>2</sup> which allow the mixing between the singlet and ( $m_s = 0$ ) quintet TT states in symmetric systems (i.e., homofission). Very recently, Weiss et al. have observed the formation of the triplet-pair quintet state in films of a tetracene derivative employing time-resolved electron spin resonance.<sup>160</sup> The

formation of the quintet state emerging from singlet fission has also been detected in pentacene dimers by Tayebjee and co-workers<sup>161</sup> and Basel et al.<sup>162</sup> combining electron spin resonance with transient absorption measurements.

At large spatial separation the electronic coupling between the two triplets vanish and the TT states with different spin multiplicities become degenerate. In this situation, the wave function of the multiexciton singlet state acquires pure  $^1\text{TT}$  character (eq 18), with no mixing to other configurations. Although the two triplets are electronically decoupled, they are not completely independent since spin entanglement remains and decoherence<sup>163–165</sup> is necessary in order to produce fully independent triplets,<sup>69,72,155</sup> in which each individual triplet loses the information regarding the spin of the paired triplet. Spin coherence in organic materials can be rather stable,<sup>71,160,161</sup> but it is eventually lost via finite temperature effects, energetic disorder, and dynamics disorder (exciton–phonon coupling).<sup>159,166</sup> The loss of spin coherence through interaction with the environment is crucial to understand the fate of the generated triplets. As a result of quantum decoherence, the spins of the two triplets are no longer coupled and their overall spin state corresponds to a statistical average of  $^1(\text{T}\cdots\text{T})$ ,  $^3(\text{T}\cdots\text{T})$ , and  $^5(\text{T}\cdots\text{T})$  states.

Since the  $^1\text{TT}$  state corresponds to the concomitant excitation of two electrons (two electron–hole pairs), its computational characterization requires the use of electronic structure models able to deal with doubly excited configurations. Therefore, standard linear response single reference<sup>167</sup> approaches for the computation of electronic transitions<sup>167</sup> cannot be used, even qualitatively, for its calculation. In particular, the commonly available implementations of the successful time-dependent density functional theory (TDDFT)<sup>168</sup> for finite systems cannot treat transitions beyond single excitation character since these are based on linear response theory in the adiabatic local-density approximation (ALDA).<sup>169–171</sup> Furthermore, the diradical (or diradicaloid) character of many of the chromophores potentially interesting for singlet fission recommends the use of the multiconfigurational family of approaches in order to properly describe the electronic structure of the ground and low-lying excited states.

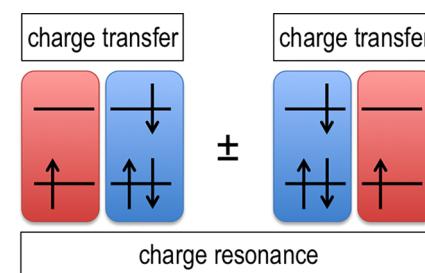
The  $^1\text{TT}$  state was computationally characterized for the first time by Zimmerman et al. in the study of the singlet fission mechanism in pentacene.<sup>118</sup> Ab initio calculations at the complete active space self-consistent field (CASSCF)<sup>172–174</sup> and multireference Møller–Plesset perturbation theory (MRMP)<sup>175–177</sup> level on a dimer model identified a dark singlet state with double excitation character as the potential multiexcitonic singlet fission precursor. Moreover, the authors found that the PES of the  $^1\text{TT}$  state crosses  $S_1$  at short intermolecular distances. The multiexciton character of the  $^1\text{TT}$  state and its interaction to  $S_1$  in tetracene and pentacene crystals was further explored<sup>138</sup> by means of the restricted active space spin-flip (RAS-SF) approach.<sup>178</sup> This approach has demonstrated very good performance in the characterization of the  $^1\text{TT}$  state in a variety of singlet fission systems,<sup>135,156,179–183</sup> and together with CASSCF, multireference perturbation theory corrections and other highly correlated methods have become standard methodologies in the electronic structure study of singlet fission in oligomer-based models.<sup>103–105,121,135,184–190</sup> Despite the success of these calculations in describing the electronic structure intricacies of singlet fission states, novel ideas are desired in order to mitigate their computational load, specially in the characterization of

ME states in the presence of several chromophores, where the computational cost of active space based methods grows exponentially. In this sense, recently a computational approach has been proposed for the computation of  $^1\text{TT}$  wave functions based on the construction of a spin-Heisenberg–Dirac–Van Vleck Hamiltonian by means of single excitation spin-flip calculations from a high-spin reference.<sup>191</sup>

In contrast to the delocalization degree of  $S_1$  in molecular crystals, the  $^1\text{TT}$  state is expected to be strongly localized on two chromophores since its electronic structure can be approached (in many cases) as two weakly interacting triplets. The different tendency toward delocalization of  $^1\text{TT}$  and  $S_1$  has been computationally described in the study of singlet fission in crystal tetracene<sup>103,192</sup> and in covalent dimers.<sup>181</sup> The localized nature of the triplet-pair state on two chromophores has justified the use of dimer-based models for the computational study of  $^1\text{TT}$  in extended systems. On the other hand, the experimentally measured fast diffusion of the triplet-pair in crystal tetracene<sup>193</sup> suggesting cooperative singlet–triplet exciton transport pinpoints the need to go beyond the dimer model in order to achieve a more complete picture of the singlet fission process.

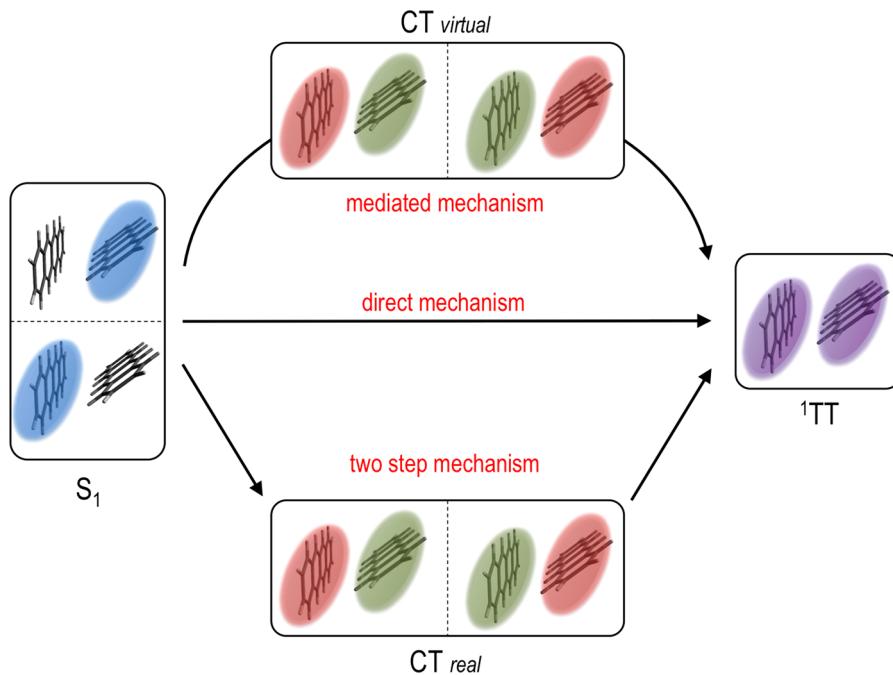
The computational evaluation of the  $^1\text{TT}$  nature of adiabatic wave functions is not trivially achieved. The multiexciton characterization has been done using a variety of computational tools and approaches, such is the quantification of double excitations,<sup>180,186,194</sup> by employing localized molecular orbitals<sup>106,121,181,192,195</sup> or through the use of the local spin concept.<sup>196,197</sup>

**3.2.4. Charge Transfer/Resonance States.** In the adiabatic electronic states of chromophore dimers, aggregates, or molecular solids, the localized single excitons and multiexcitons such as  $^1\text{TT}$  tend to mix with charge transfer (CT) and/or charge resonance (CR) configurations. Notice that while CT states (also called Wannier-Mott in solid state physics<sup>15</sup>) indicate to some extent a net charge displacement (spatially separated electron/hole pairs), the CR term, typical of symmetric arrangements of chromophoric units, refer to the presence of charged configurations describing the ionic nature of the electronic wave function but do not imply a permanent charge separation (Figure 4).<sup>198</sup>



**Figure 4.** Representation of charge transfer (CT) and charge resonance (CR) configurations for a pair of chromophores.

The involvement of CT or CR states in singlet fission has been a central topic of debate,<sup>41,103,111,118,121,135,138,186,199–203</sup> and its role has been a key element in order to distinguish between different potential fission electronic mechanisms in the formation of  $^1\text{TT}$  (Figure 5): (i) direct internal conversion from  $S_1$  to  $^1\text{TT}$  (no involvement of CT states), (ii) singlet fission mediated by CT states (CT as virtual states assisting the formation of  $^1\text{TT}$  in a superexchange mechanism), or (iii)



**Figure 5.** Proposed mechanisms for the formation of  ${}^1\text{TT}$  in relation with the involvement of CT states.

sequential two one-electron transfer steps with CT state as a real intermediate effectively populated prior to the generation of the triplet-pair.

The low-lying singlet excitons in covalent dimers, aggregates or molecular solids can contain some CT/CR character. The weight of the CT configurations in the adiabatic wave function of  $S_1$  is strongly linked to the relative energy of CT with respect to FE states and the interchromophoric couplings. In some cases, the CT state has even been suggested as the lowest excited singlet state.<sup>185</sup> Relatively low-energy CT states combined with nonvanishing interchromophore couplings induces sizable mixings between CT and FE configurations and has been related to the magnitude of the Davydov splitting in absorption spectra<sup>203,204</sup> and to the extent of exciton delocalization.<sup>111,122,139</sup> On the other hand, molecular crystals with high-lying CT states result in very weak FE/CT mixing and larger localization of the  $S_1$  exciton.<sup>148</sup> The mixing of CT configurations with  ${}^1\text{TT}$  is, in general, much lower than for  $S_1$  and higher singlet states ( $S_n$ ), and has a much weaker impact on its energy and electronic properties. As discussed, the different ability of  $S_1$  and  ${}^1\text{TT}$  to mix with CT configurations has been related to the much larger spatial extension of the former,<sup>103,181,192</sup> and to the magnitude of the binding energy of the two triplets (eq 25).

The coupling of CT configurations with  $S_1$  and  ${}^1\text{TT}$  states has been commonly associated with the singlet fission mediated mechanism. In fact, this is the most accepted path for singlet fission in extended systems, such as crystal tetracene and pentacene.<sup>3,41,107,121,203</sup> On the other hand, CT states in weakly coupled covalent dimers of pentacene have been calculated at rather high relative energies, suggesting a minor role of CT configurations and the preference for direct  $S_1 \rightarrow {}^1\text{TT}$  mechanism for the intramolecular singlet fission in these dimers.<sup>105</sup>

Computational characterization of the CT or CR mixing in adiabatic wave functions might be a non trivial task, in particular for CR contributions in symmetric systems where the

measure of the static dipole moment of the state is not appropriate<sup>205</sup> and diabatization schemes<sup>206–212</sup> or decomposition techniques<sup>192,195,213</sup> are required. The need for the characterization and quantification of CT content in electronic transitions has generated a variety of computational techniques.<sup>214–216</sup> The CT nature of  $S_1$  can be assessed by standard charge population analysis, spatial overlap measure between ground and excited states,<sup>217</sup> by means of the attachment/detachment density analysis,<sup>218</sup> or employing other tools for the quantitative analysis of excited states.<sup>219</sup> The characterization of electronic excitations in systems with multiple chromophoric unities can be easily obtained through the construction of natural transition orbitals (NTOs).<sup>141</sup> Analysis of NTOs between ground and an excited state provides a visual representation of the spatial localization of the hole and electron and can be used to quantify the participation of each atom in the transition. On the other hand, the use of simple tools such as NTOs are not of much use when trying to quantify or even identify the presence of CR contributions with no net charge separation, and more refined strategies need to be applied.<sup>125,220–229</sup> The difficulty to evaluate the participation of CR configurations in excitonic states from ab initio calculations has arguably led to underestimate their involvement in the singlet fission of pentacene.<sup>138</sup>

A straightforward strategy to explore the role of CT states in singlet fission is the direct computation of diabatic energies and wave functions. The energy of CT or CR configurations within the dimer model can be roughly approximated as the interaction of oxidized and reduced chromophores:

$$E(\text{CT}) \approx \text{IP} - \text{EA} + C \quad (26)$$

where IP and EA are the molecule's ionization potential and electron affinity, respectively, and C is inversely proportional to the charge separation distance. The expression in eq 26 can be used semiquantitatively at best, since it only takes into account the Coulomb interaction between charges and completely disregards orbital contribution terms.

A more refined approach toward the computation of CT states can be achieved with the constrained DFT (C-DFT) method,<sup>230</sup> where constraints on the charge localization are applied during the self-consistent field calculation to force negatively and positively charged densities on individual chromophores. The C-DFT method has been employed to evaluate the relative energy of CT states in several singlet fission systems<sup>94,135,181,231,232</sup> and to show how CT states in crystal pentacene are largely stabilized through electrostatic screening and the formation of electronic bands.<sup>233</sup>

**3.2.5. Excimer.** An excimer is an electronic state of a homodimer resulting from the interaction of an excited monomer with another monomer with the same atomic structure in the ground state. Usually, excimer formation conduces to considerable depletion of photoluminescence and large redshift of the fluorescent band, that no longer exhibits vibronic resolution.<sup>234</sup> Excimer formation is attained through nuclear relaxation driven by intermolecular exciton interaction and charge resonances,<sup>235</sup> resulting in strong mixing of LE and CR states.<sup>236</sup> Due to the large stabilization energy of the excimer with respect the asymptotic (molecular) excited state, excimers have been also referred to as self-trapping states.<sup>237,238</sup>

The role of excimers or excimer-like states in singlet fission is not completely solved. Several studies have suggested that excimers might catalyze the formation of the triplet-pair state. In this sense, the excimer state has been proposed as a precursor intermediate between the S<sub>1</sub> and <sup>1</sup>TT states in crystal pentacene<sup>118</sup> and in derivatives of diketopyrrolopyrrole<sup>91,239,240</sup> and terrylene<sup>241</sup> and as an intermediary state populated after the formation of the triplet-pair in perfluoropentacene.<sup>242</sup> Formation of excimers seems to facilitate the singlet fission process in dilute solutions of tetracene and pentacene.<sup>112,154</sup> Recently, Feng and Krylov have concluded that excimer formation along the relaxation of S<sub>1</sub> in tetracene dimers enhances the rate formation of <sup>1</sup>TT (first step in eq 2) but hinders the triplet-pair dissociation toward free triplets (second step in eq 2).<sup>182</sup> On the other hand, the lack of singlet fission in face-to-face tetracene covalent dimers has been attributed to the formation of a very stable excimer state acting as a trap state and hindering the formation of <sup>1</sup>TT.<sup>183</sup> Similarly, molecular packing in crystal peropyrrene results in the formation of low-energy excimer states and largely endothermic singlet fission energy.<sup>243</sup> Decay of excitons in pentacene films has been attributed to ultrafast excimer formation competing with singlet fission.<sup>244,245</sup> Moreover, excimer formation has been associated with the lack of temperature dependence in the generation of the <sup>1</sup>TT state in tetracene and strong temperature dependence for the triplet-triplet dissociation step.<sup>246</sup>

## 4. SINGLET FISSION RATES

### 4.1. Rate Models

The kinetics of the singlet fission photophysical process can be modeled as a first-order reaction. In the limit of weak coupling between initial and final states, the rate constant for the singlet fission reaction can be expressed by the Fermi's golden rule (FGR):<sup>247</sup>

$$k_{\text{FGR}} = \frac{2\pi}{\hbar} |V|^2 \delta(E_i - E_j) \quad (27)$$

where V is the coupling between initial and final states, and  $\delta(E_i - E_j)$  guarantees energy conservation along the process, which is typically formulated as the Franck–Condon weighted density

of states (FCWD).<sup>248</sup> The general rate expression in eq 27 has been discussed in detail regarding the importance of electronic coupling within the diabatic basis in the seminal reviews by Smith and Michl.<sup>2,3</sup>

In the high temperature limit, the FCWD term in eq 27 can be classically approximated to the celebrated Marcus non-adiabatic expression for electron transfer rate<sup>249</sup> (eq 28),

$$k_{\text{Marcus}} = \frac{2\pi}{\hbar} |V|^2 \frac{1}{\sqrt{4\pi\lambda kT}} e^{-(\Delta G + \lambda)^2 / 4\lambda kT} \quad (28)$$

where  $\lambda$  is the reorganization energy and  $\Delta G$  the Gibbs free energy difference between initial and final states. The rate expression in eq 28 has been applied to evaluate the singlet fission rates and yields in crystals of PDI derivatives.<sup>86</sup> These results disregard the indirect (two steps) one-electron pathway as a viable fission mechanism in PDI due to too large energy for the CT states. The Marcus theory has been also applied to explore the interplay between CT-mediated singlet fission mechanism and the role of excimer formation in rylene and diketopyrrolopyrrole derivatives.<sup>240</sup> Depending on the relative energy of the CT state either the supereexchange mechanism (lower CT) or the excimer-mediated path (higher CT) prevails.

The nonadiabatic Marcus rate constant approximation is not valid for large couplings. This limitation can be overcome by means of the simple Bixon-Jortner (BJ) expression<sup>250–252</sup> (eq 29), which extends the low-frequency approach to the adiabatic limit by including noninstantaneous solvation dynamics triggered by electron transfer,

$$k_{\text{BJ}} = \sum_n \frac{|V|^2 k_n}{1 + \tau_n^{\text{ad}} |V|^2} \quad (29)$$

where

$$k_n \equiv \left( \frac{\pi}{\hbar^2 \lambda kT} \right)^{1/2} |\langle 0 | n \rangle|^2 e^{-(\Delta G + n\hbar\omega + \lambda)^2 / 4\lambda kT};$$

$$\tau_n^{\text{ad}} \equiv \frac{4\pi}{\hbar\lambda} \tau_{\text{ad}} |\langle 0 | n \rangle|^2 \quad (30)$$

$\tau_{\text{ad}}$  is the adiabatic time scale corresponding to the solvent's relaxation time, and  $\omega$  is the frequency of the primary mode. In singlet fission, contrary to electron transfer systems, induced changes in the long-range dielectric polarization are expected to be rather weak, resulting in short relaxation times. In that scenario, eq 29 effectively converges back to the Marcus expression with a vibronic progression. Yost et al. used the BJ model to estimate and compare the fission rates in a variety of acene derivatives.<sup>94</sup> To that end, they combined experimental data with C-DFT electronic energies and couplings between diabatic states to analyze trends in singlet fission rates. The study highlights the importance of CT mixings in the bright state, which can significantly increase the electronic couplings to the triplet-pair state. Moreover, correlation between couplings and rates was employed to identify the separation between nonadiabatic (weak coupling) and adiabatic (strong coupling) regimes. In the former, the singlet fission rates exhibit a quadratic relationship with the electronic coupling, while in the adiabatic regime the rate is not sensitive to an increase of the coupling. Interestingly, based on the coupling-rate relationship, the authors concluded that although the dimer model can be largely inaccurate in the computation of electronic couplings in molecular crystals (specially in the strong coupling cases), it is a reliable approach to predict fission rates.

With consideration of the nature of the singlet fission mechanism, which involves minor charge distribution changes and weak perturbation of the environment, it seems more appropriate to employ energy transfer rate expressions instead of electron transfer theories (e.g., Marcus and Bixon-Jortner equations). Concretely, singlet fission rates can be estimated using the Förster energy transfer theory<sup>253</sup> for the triplet energy transfer,<sup>68,248</sup> in which the FCWD is replaced by an overlap of density of states  $J$  (eq 31).<sup>254</sup> This approach has been employed by Yang and Hsu to predict singlet fission rates in pentacene,<sup>255</sup> obtaining lifetimes in the subpicosecond range, in good agreement with experimental measurements.<sup>153,256</sup>

$$k_{\text{TET}} = \frac{2\pi}{\hbar} |V|^2 J \quad (31)$$

The nonadiabatic transition between two states can be approached by the Landau–Zener formulation and its extension by Stueckelberg to include quantum tunneling<sup>257–260</sup>

developed in the early 1930's. The Landau–Zener–Stueckelberg (LZS) equation for the rate constant of the transition takes the general form:

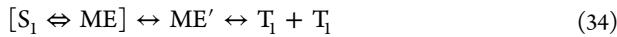
$$k_{\text{LZS}} = \frac{\omega}{2\pi} 2(1 - P)P \quad (32)$$

where  $\omega$  is the frequency of the vibrational mode assisting the transition and  $P$  denotes the transition probability, which can be expressed in terms of excess energy, the electronic coupling, and the slopes of the states at the crossing point. Despite the limitations of the initial LZS models, the theory has been largely expanded to simulate transitions with energies near or lower than the crossing point, to cover for the entire range of electronic couplings, account for quantum mechanical tunneling effects, or deal with multichannel and multidimensional problems.<sup>261–263</sup> In particular, the fact that LZS approach is valid for any value of the coupling makes it very appealing for the study of the singlet fission process. The LZS model has been used in combination with multireference electronic structure calculations to evaluate the transition probability from  $S_1$  to  ${}^1\text{TT}$  in pentacene.<sup>118,138</sup> The probabilities obtained suggest that intermolecular distortions might induce fast (subpicosecond time scale) nonadiabatic transition to the multiexciton state.

Chan et al.<sup>264</sup> have applied the harmonic transition state theory (HTST)<sup>265</sup> to the study of singlet fission in crystalline tetracene. In their kinetic model (eq 33), the ratio of the product of the vibrational modes was approximated by an effective attempt frequency  $\nu_0$ .

$$k_{\text{HTST}} = \nu_0 e^{-\Delta G^\# / kT} \quad (33)$$

In their study, the authors took the activation energy  $\Delta G^\#$  as the energy difference between  $S_1$  and the intermediate multiexciton state, labeled in their work as ME', that results upon relaxation of the photoexcited state corresponding to a coherent superposition of  $S_1$  with a higher ME state, and that eventually splits into two independent triplets (eq 34) due to the loss of spin coherence.



The photophysical reaction in eq 34 introduced a new potential mechanism for singlet fission where endoenergy can be overcome by coherent population of a higher ME state, hence avoiding the need for thermal activation.

Feng et al. have developed a simple kinetic model based on transition state theory to specifically evaluate the rates of singlet fission.<sup>156</sup> This approach considers a reaction between three (adiabatic) states [i.e., the initially excited state ( $S_1$ ), the triplet-pair singlet ( ${}^1\text{TT}$ ), and the two uncoupled triplets ( $T_1$ )]. Therefore, the model divides the fission kinetics in two steps ( $S_1 \rightarrow {}^1\text{TT}$  and  ${}^1\text{TT} \rightarrow 2T_1$ ) and uses the linear free energy approach<sup>266,267</sup> to account for activation energy.

$$k[S_1 \rightarrow {}^1\text{TT}] \approx |V|^2 e^{-\alpha \Delta G_{\text{SF}} / kT} \quad (35)$$

$$k[{}^1\text{TT} \rightarrow 2T_1] \approx e^{-\alpha \Delta G_b / kT} \quad (36)$$

The rate expressions for the two reaction steps are shown in eqs 35 and 36, where  $\alpha$  is the coefficient corresponding to the linear free energy approach,  $\Delta G_{\text{SF}}$  is the free energy difference between  $S_1$  and  ${}^1\text{TT}$  states,  $\Delta G_b$  is the binding energy of two triplets, and  $V$  is the coupling expressed in the basis of adiabatic states and corresponds to the nonadiabatic matrix coupling (NAC). In their model, the authors avoid the explicit computation of NACs by employing the norm of the one-particle transition density matrix as a proxy (see section 5.2):<sup>268</sup>

$$V \approx \frac{\|\gamma\|}{\Delta E} \quad (37)$$

where  $\gamma$  and  $\Delta E$  are the one-particle transition density matrix and the electronic energy difference between initial ( $S_1$ ) and final ( ${}^1\text{TT}$ ) adiabatic states, respectively. In spite of its simplicity, and although the model should not be used to quantitatively estimate fission rates, it allows one to compare the kinetics between different singlet fission materials and study the factors that control the fission rates. In particular, the model indicates that singlet fission rate in tetracene is determined by the first step due to endothermicity and explains why it is significantly faster in pentacene than in tetracene, in agreement with experimental measurements.<sup>35,94,245,256,264,269–272</sup> On the other hand, it predicts faster singlet fission in hexacene compared to pentacene in contradiction to experimental measurements.<sup>273</sup> The model has been also applied to study the relative rates of singlet fission in different crystal forms of 1,3-diphenylisobenzofuran, 1,6-diphenyl-1,3,5-hexatriene, and 5,12-diphenyltetracene<sup>179</sup> and in covalent dimers of tetracene.<sup>181–183</sup> All these studies converge in the idea that efficient singlet fission requires a balanced equilibrium between the triplet–triplet binding energy and the driving force for the overall process.

#### 4.2. Role of Entropy

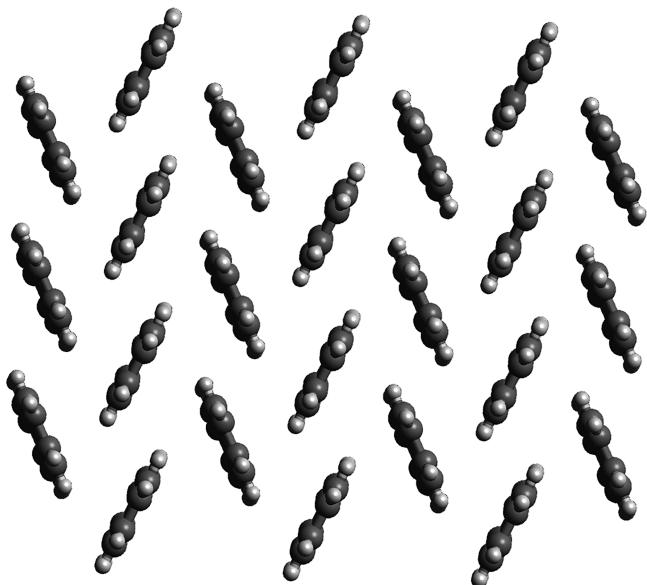
Early works on singlet fission have largely overlooked the impact of entropic contributions, but several investigations on the kinetics of the process have noted the possibility of entropy promoting singlet fission. Despite these efforts, it is still not completely clear how entropy is involved in the fission process and this issue deserves more attention. In particular, there is some controversy about the role of entropy in the case of endothermic singlet fission reaction, with the study of singlet fission kinetics in tetracene being a paradigmatic example.<sup>274</sup> The lack of temperature dependence on the decay of  $S_1$  in tetracene<sup>246,264,270,271,275</sup> has been related to the presence of a rather stable intermediate state, probably the triplet-pair singlet, by several authors,<sup>246,270,271</sup> while others have noticed the potential importance of entropic effects.<sup>156,264</sup> These two rationalizations are not necessarily incompatible if one considers a two-step reaction, since a low-energy intermediate

provides a deactivation path for  $S_1$  with no activation barrier, while entropy could be the most important factor in the separation of the two triplets.

The importance of entropic factors was first noticed by Chan and collaborators,<sup>264</sup> who, using the rate expression in eq 33, discussed how entropic gain is the main driving factor for the decoupling of the multiexciton state into two independent triplets, suggesting that entropy is eventually responsible for overcoming the singlet fission endothermicity in tetracene. These results would also explain why molecular dimers of tetracene and pentacene give much lower fission efficiencies than their crystalline forms.<sup>183</sup> The entropic gain at the transition (ME') state can be quantified as

$$\Delta S^\neq = k_B \ln \frac{\Omega(ME')}{\Omega(S_1)} \quad (38)$$

where  $\Omega(S_1)$  and  $\Omega(ME')$  are the number of configurations available for each of the two states. By considering that the fission process takes place within the *ab* plane of crystalline tetracene (Figure 6),<sup>204</sup> one arrives at an expression for the



**Figure 6.** Crystal structure of tetracene and pentacene along the *ab* plane.

entropy difference in terms of the temperature-dependent number of tetracene molecules explored by the  $S_1$  state through exciton diffusion,<sup>276</sup>

$$\Delta S^\neq = k_B \ln(3\pi\rho l_D^2 - 1) \quad (39)$$

where  $\rho$  is the area density of tetracene molecules in the *ab* plane ( $\rho = 4.086 \text{ nm}^{-2}$ ) and  $l_D$  is the temperature-dependent exciton diffusion length.

The relevance of entropy in the singlet fission process has also been illustrated and rationalized by the two-step kinetic model in eqs 35 and 36. By employing arguments related to the electronic delocalization degree for the three adiabatic states considered ( $S_1$ ,  ${}^1\text{TT}$ , and  $T_1$ ) to evaluate relative number of microstates, it is shown that entropy increases in both steps (eq 2). The entropy gain in the first step can be related to the initial delocalization of  $S_1$  and the following dimer localization of  ${}^1\text{TT}$  state. Because the multiexciton can evolve into multiple pairs of triplet states, entropy also increases in the  ${}^1\text{TT} \rightarrow 2T_1$  reaction.

These results directly connect entropy with material structure. Structural morphology has been long recognized to have a major role in singlet fission by controlling electronic couplings (see section 5). Moreover, morphology also influences singlet fission through entropy by tuning the range of exciton delocalization and establishing the number of available  ${}^1\text{TT}$  and  $T_1$  microstates.

## 5. COUPLINGS IN SINGLET FISSION

The FGR expression in eq 27 links the rate of the fission process to the coupling  $V$  between the initial and final states. This relationship has motivated the computation of  $V$  in order to evaluate, rationalize, and predict reaction rates, mainly for the formation of the  ${}^1\text{TT}$  state from the initially excited state. Moreover, the magnitude and characterization of these electronic couplings can be employed to identify the physical nature of the fission process and ultimately identify the key structural and electronic parameters controlling the kinetics of the photophysical reaction.

### 5.1. Electronic Couplings

Within the diabatic picture, the dynamics of electronically activated molecular systems is controlled by the interactions between the electronic states (eq 15), which are coupled through the electronic Hamiltonian:

$$V_{IJ} = \langle \Xi_I(\mathbf{R}) | H_{el} | \Xi_J(\mathbf{R}) \rangle \quad (40)$$

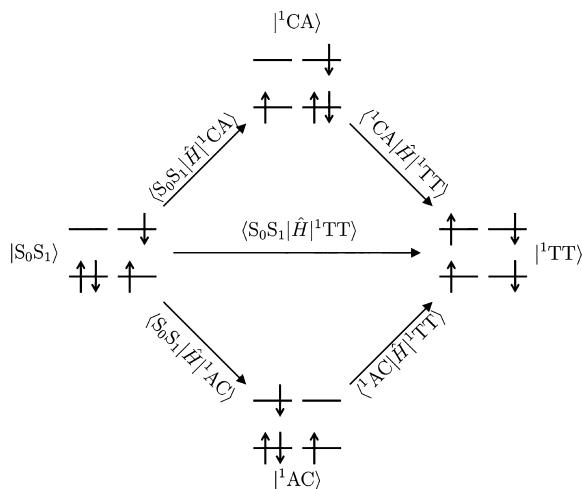
$V_{IJ}$  is the diabatic coupling often also termed as electronic coupling. The term singlet fission coupling is sometimes used in the singlet fission literature,<sup>255</sup> referring to the specific coupling between the diabatic singlet exciton and the triplet-pair ( ${}^1\text{TT}$ ). Determination of the magnitude of electronic couplings in different singlet fission materials and its dependence with respect to interchromophoric arrangement has become a central element in the computational modeling of singlet fission, which has been employed to discuss and identify potential mechanisms and to approximate absolute or relative fission rates.

It is important to note that the rate expression in eq 27 corresponds to the lowest order term in the expansion of the state-to-state transition. Expansion to the next order results in

$$k = \frac{2\pi}{\hbar} \left| V_{if} - \sum_{m \neq i,f} \frac{V_{fm} V_{mi}}{E_m - E_i} \right|^2 \delta(E_i - E_f) \quad (41)$$

where  $i$  and  $f$  indices indicate initial and final electronic states, typically the lowest local exciton, related to the lowest excited singlet of the monomer, and the (diabatic)  ${}^1\text{TT}$  state, respectively. Actually, this type of rate expression was already used in early investigations on singlet fission.<sup>6</sup> The  $O(V^2)$  term, which includes the sum over  $m$ -intermediate states, corresponds to virtual transitions to other states and can become important if  $V_{fm}$  and  $V_{mi}$  are large for some  $m$ -state which is not too high in energy with respect to initial and final states. In particular, the second-order contribution might play a major role when the first-order contribution is small ( $V_{if} \sim 0$ ). Eq 41 provides the theoretical background to rationalize the fission mechanism in terms of direct (1st-order) or mediated (2nd-order) interactions.<sup>3</sup> In many occasions the term superexchange has been used to refer to the mechanism involving virtual intermediate states, which are never directly populated but assist the transition. The potential intermediate states in the singlet fission case are of the CT nature. Since the direct

coupling between the  $S_1$  monomer localized (pure Frenkel character) and  $^1\text{TT}$  states involves a two-electron change, the computed  $V_{ij}$  dictated by two-electron integrals, are usually relatively small (a few meV). On the other hand, the interactions of  $S_1$  and  $^1\text{TT}$  with CT configurations correspond to one-electron processes with couplings typically 2 orders of magnitude larger than the direct one (Figure 7).



**Figure 7.** Diagrammatic representation of singlet fission process by the HOMO–LUMO dimer model. CT configurations are indicated as anion–cation ( $^1\text{AC}$ ) and cation–anion ( $^1\text{CA}$ ) spin singlets.

Numerical evaluation of direct and mediated couplings for different singlet fission materials and with different computational methodologies show that, as a general rule, the mediated interaction is more efficient than the direct one, even when the CT mediator states lie rather high in energy.

$$|\Xi_i\rangle = \sum_{k=0}^{\infty} |\Xi_i^{(k)}\rangle; |\Xi_f\rangle = \sum_{k=0}^{\infty} |\Xi_f^{(k)}\rangle \quad (42)$$

It is important to note that the second-order expression for the FGR (eq 41) can be derived by applying perturbation theory to the initial and final states (eq 42). Since the first-order correction to the diabatic states is linear with the perturbation  $V$ :

$$|\Xi_i^{(1)}\rangle = - \sum_{m \neq i} \frac{V_{mi}}{E_m - E_i} |\Xi_m\rangle \quad (43)$$

$$\langle \Xi_i | V | \Xi_f \rangle = V_{if} - \sum_{m \neq i,f} \frac{V_{fm} V_{mi}}{E_m - E_i} + O(V^3) \quad (44)$$

This path to eq 41 has a clear connection to those approaches that include some CT character on the diabatic (or quasi-diabatic) states and that do not make use of the direct and mediated terminology. In a more general view, the perturbative expansion relates the superexchange phenomena with the mixing of CT (or CR) configurations in the adiabatic states. It is important to note that the  $(E_m - E_i)$  denominator in eqs 41, 43, and 44 considers degeneracy between initial and final states ( $E_f = E_i$ ). Otherwise, the  $E_m - (E_i + E_f)/2$  denominator can be used instead.

The question about what is the optimal coupling for efficient singlet fission is of vital importance. Despite that one might expect electronic couplings to be system-dependent, several

studies have shown that it is possible to establish general rules within the conformational space of two weakly interacting molecules.<sup>277</sup> In this sense, the cofacial slip-stacked arrangement between  $\pi$ -conjugated chromophores is, in general, considered as the optimal disposition for singlet fission couplings.<sup>242,278,279</sup> Other intermolecular configurations might also result in favorable  $S_1/{}^1\text{TT}$  interactions for electronic couplings and fission rates, like in the tilt orientation between molecular pairs in the herringbone structure of tetracene and pentacene crystals, or the in-plane arrangement in 1,3-diphenylisobenzofuran crystals.<sup>179</sup>

On one hand, from the FGR rate equation one is tempted to deduce that stronger couplings will produce faster and more efficient singlet fission. But, on the other hand, too strong couplings might open alternative deactivation channels; such is induced charge separation or excimer formation,<sup>85,182,280–282</sup> eventually resulting in lower fission efficiencies. But, even more importantly, electronic coupling tends to further stabilize the monomer singlet than the triplet state, which can lower the fission driving force or even put the lowest singlet quite below twice the triplet energy, resulting in highly endothermic fission process.<sup>283</sup> Even in the case where the system populates the  ${}^1\text{TT}$  state, too strong interchromophore coupling might result in strong triplet–triplet interaction and large stabilization of the triplet-pair coupled into a singlet state [i.e.,  $E({}^1\text{TT}) \ll E({}^3\text{TT})$ ], effectively blocking the formation of two independent triplets. A paramount example of this situation is the low-lying  $2^1\text{A}_g$  dark state of *trans*-butadiene, which holds a doubly excited electronic structure that can be expressed as two strongly coupled triplets each one occupying one of the two ethylene units.<sup>284–287</sup> Hence, in a good singlet fission material, a compromise must be reached in order to hold not too weak but not too strong electronic coupling.

**5.1.1. Computation of Electronic Couplings.** Quantification of electronic couplings between chromophores has been related to the energy separation between the two lowest excited singlet states in dimers, that is the Davydov splitting,<sup>288</sup> but this quantity is not directly related to the singlet fission coupling and should be only used as a first qualitative approximation. The evaluation of electronic couplings relies on the computation of off-diagonal terms of the diabatic Hamiltonian (eq 40). There are many different approaches in the literature that simplify the computation of  $V_{ij}$  by avoiding the computation of one- or two-electron interaction integrals and/or the explicit construction of diabats<sup>289,290</sup> and several of such approximations have been applied to the singlet fission problem.

The coupling term has been often related to the electron transfer integral, hopping integral, or resonance integral used in the context of charge transport models.<sup>216</sup> A very simple approach to the computation of transfer integrals is obtained by the use of the Koopman's theorem as the half energy splitting of frontier orbitals within the dimer model:<sup>291</sup>

$$t_H \approx \frac{\epsilon_{\text{HOMO}} - \epsilon_{\text{HOMO}-1}}{2}; t_L \approx \frac{\epsilon_{\text{LUMO}+1} - \epsilon_{\text{LUMO}}}{2} \quad (45)$$

where  $\epsilon_i$  are the orbital energies of the dimer, and  $t_H$  and  $t_L$  are the one electron couplings for the monomer HOMO (transfer of holes) and LUMO (transfer of electrons), respectively. In singlet fission,  $t_H$  and  $t_L$  in eq 45 can be used as proxies for the computation of couplings between low energy locally excited

singlet and CT states.<sup>292</sup> It is important to note that this very simple approach is only valid for orbitals close in energy. A slightly more sophisticated approach is the one from Longuet-Higgins and Roberts,<sup>293</sup> which assumes a linear relationship between the interstate interaction and orbital overlap  $S_{IJ}$  (eq 46). Such a model has been used in the study of organic dimers, but systematic computational analysis of molecular dimers indicates that there is no linear correlation between orbital overlaps and electronic couplings,<sup>182</sup> advising against the use of eq 46 for quantitative purposes.

$$V_{IJ} \approx kS_{IJ} \quad (46)$$

Probably the most well-known scheme to the computation of electronic couplings in singlet fission is the one described by Michl et al. in the 2010 and 2013 review papers,<sup>2,3</sup> in which the diabatic wave functions in a bichromophoric system are described by single Slater determinants and assume the frozen orbital approximation in which the interacting states only differ by the occupancies of the two HOMO/LUMO orbital pairs on each molecule. Then, the couplings between the low-lying configurations are described as

$$\langle S_1 S_0 | \hat{H} | ^1\text{TT} \rangle = \sqrt{3/2} [(l_A l_B | h_B l_A) - (h_A h_B | l_B h_A)] \quad (47)$$

$$\langle ^1\text{CA} | \hat{H} | S_1 S_0 \rangle = (l_A | \hat{F} | l_B) + 2(h_A l_A | l_B h_A) - (h_A l_A | h_B l_B) \quad (48)$$

$$\langle ^1\text{CA} | \hat{H} | S_0 S_1 \rangle = -(h_A | \hat{F} | h_B) + 2(h_B l_B | l_B h_A) - (h_B l_B | h_B l_B) \quad (49)$$

$$\langle ^1\text{CA} | \hat{H} | ^1\text{TT} \rangle = \sqrt{3/2} [(l_A | \hat{F} | h_B) + (l_A l_B | h_B l_B) - (l_A h_A | h_B h_A)] \quad (50)$$

$$\langle S_1 S_0 | \hat{H} | S_0 S_1 \rangle = 2(h_A l_B | l_A h_B) - (h_A l_B | h_B l_A) \quad (51)$$

where  $h$  and  $l$  correspond to HOMO and LUMO orbitals of the monomer, and subindices  $A$  and  $B$  indicate different chromophores. Expressions 47–51 consider mutually orthogonal frontier molecular orbitals that is,  $S_{ij} = \delta_{ij}$ , the  $(ij|\hat{F}|lj)$  term is the matrix element of the Fock operator and  $(ijkl)$  a two-electron integral between spatial orbitals:

$$(ijkl) \equiv \int \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) r_{12}^{-1} \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2) \quad (52)$$

This approach has been systematically employed in the search for optimal couplings in singlet fission<sup>279,283</sup> and to build effective Hamiltonians to explore the fission dynamics. Moreover, the simple interstate couplings in such approximation highlight the two-electron nature of electronic coupling for the direct mechanism (i.e., potentially weak), while one-electron contributions for the couplings to  $^1\text{CA}$  and  $^1\text{AC}$  configurations suggest, in general, larger couplings for singlet fission mediated by CT states or for the two step mechanism with the formation of CT intermediates. The extension of this simple method to coupling expressions taking into account nonorthogonality between monomeric HOMOs and LUMOs has been presented elsewhere.<sup>279</sup>

In general, the direct computation of electronic couplings between localized excited states is referred to as the direct coupling (DC) scheme,<sup>295</sup> which has been extensively used to calculate electron transfer couplings.<sup>296–299</sup> This approach assumes that electronic eigenstates correspond to symmetric and antisymmetric linear combinations of the initial ( $i$ ) and final ( $f$ ) diabatic wave functions, resulting in an effective electronic coupling expressed as

$$V_{\text{DC}} = \frac{H_{if} - S_{if}(H_{ii} - H_{ff})/2}{1 - S_{if}^2} \quad (53)$$

where  $S_{if}$  and  $H_{if}$  are the overlap integral and the matrix element of the electronic Hamiltonian between the two diabats, respectively. The computation of local (diabatic) excitations beyond the frozen orbital approximation (eqs 47–51) (i.e., computing low-lying eigenstates for each of the chromophoric units) can take into account correlation effects and orbital relaxation within each diabatic state, which might be very important in the description of singlet fission.<sup>110</sup> DC has been applied to evaluate singlet fission couplings in tetracene with the CASSCF approach<sup>103</sup> and very recently to the study of singlet fission in a promising biradicaloid molecule<sup>300,301</sup> in which the diabatic states are modeled with a nonorthogonal configuration interaction approach.<sup>302</sup> The computed electronic couplings for the predicted crystal structure of the molecular biradicaloid confirm its potential suitability for efficient formation of the  ${}^1\text{TT}$  state.

The methods for the calculation of electronic couplings discussed above are based on the direct construction of diabatic states. Alternatively, several approaches for the evaluation of electronic (diabatic) couplings rely on the diabatization of low-lying (adiabatic) excited states. One of these approaches is the fragment spin difference (FSD) method, typically used to evaluate couplings for triplet energy transfer processes.<sup>254,303</sup> The FSD scheme, which is a generalization of the fragment charge difference (FCD) method,<sup>304</sup> considers the coupling between diabatic states with the largest spin localization obtained as linear combinations of electronic eigenstates,

$$V_{\text{FSD}} = \frac{\Delta s_{12}(E_2 - E_1)}{\sqrt{(\Delta s_{11} - \Delta s_{22})^2 + 4\Delta s_{12}^2}} \quad (54)$$

where indices 1 and 2 refer to the computed lowest eigenstates and  $\Delta s_{ij}$  terms quantify the spin localization for the triplet states. This approach has been used for the study of diabatic couplings in polyacenes in conjunction with spin-flip CIS (SF-CIS)<sup>305</sup> eigenstates and eigenenergies.<sup>255</sup> It is worth noting that since the FSD diabatization scheme focus on the maximization of spin localization, the coupled states are not forced to hold pure LE or  ${}^1\text{TT}$  character. In other words, the diabatic states might implicitly contain CT contributions and, to a first approximation, can be seen as LE/CT and  ${}^1\text{TT}/\text{CT}$  mixings, respectively.

Finally, electronic couplings can be computed via the explicit construction of orthogonal diabatic states expressed as linear combinations of adiabats by applying a unitary transformation to the electronic eigenstates (eq 16). Then, diabatic electronic energies and couplings correspond to diagonal and off-diagonal terms of the electronic Hamiltonian, respectively. Such an approach has been used to compute pairwise couplings in  $\pi$ -conjugated molecular crystals.<sup>104</sup>

## 5.2. Derivative Couplings

In the adiabatic representation, electronic couplings vanish and the transition between states is governed by nuclei displacements through first (vectorial) and second (kinetic) derivative couplings (eq 14) (i.e., nonadiabatic couplings). Since the kinetic couplings can be expressed in terms of the vectorial couplings,<sup>306</sup> the first derivative coupling terms have deserved much attention and are typically called derivative couplings (eq 55).

$$\vec{d}_{IJ}^\alpha = \langle \Psi_I(\mathbf{R}) | \vec{\nabla}_\alpha | \Psi_J(\mathbf{R}) \rangle \quad (55)$$

Since derivative couplings correspond to the interaction between electronic degrees of freedom and distortions of the nuclear framework, they are also referred to as vibronic couplings.

Ultrafast two-dimensional electronic spectroscopy measurements have shown how vibronic coupling between  $S_1$  and  ${}^1\text{TT}$  states play a crucial role in the singlet fission dynamics and mediate ultrafast singlet fission in pentacene derivatives.<sup>307</sup> The importance of vibrational motions in the singlet fission mechanism has been further explored by Musser and co-workers with time-resolved spectroscopic measurements. Their observations indicate that strong vibronic couplings induce ultrafast internal  $S_1 \rightarrow {}^1\text{TT}$  conversion.<sup>140</sup> Computationally, the role of intra and interchromophoric distortions in singlet fission has been extensively studied with a variety of electronic structure calculations<sup>105,121,135,138,308</sup> and dynamical simulations.<sup>104,202,309,310</sup>

The direct expression for derivative couplings is almost never explicitly used in practical calculations,<sup>311–316</sup> and the relation in eq 56 obtained by means of the Hellman-Feynman theorem is employed instead.

$$\langle \Psi_I(\mathbf{R}) | \vec{\nabla}_\alpha | \Psi_J(\mathbf{R}) \rangle = \frac{\langle \Psi_I(\mathbf{R}) | \vec{\nabla}_\alpha H_{\text{el}} | \Psi_J(\mathbf{R}) \rangle}{E_J - E_I} \quad (56)$$

The equivalence in eq 56 highlights that derivative couplings will be large for small interstate energy gaps (i.e., near avoided crossings) and diverge at state crossings (i.e., conical intersections). The formalism for the computation of nonadiabatic couplings was initially developed in the frame of multiconfigurational SCF and multireference CI wave functions<sup>311–313,317–319</sup> and later on for single reference CIS,<sup>315,320</sup> coupled-cluster wave functions,<sup>208,321,322</sup> and for the TDDFT method.<sup>316,320,323–325</sup> In spite of all these efforts, it is safe to say that the calculation of derivative couplings is not available for most of the excited state approaches in many of the quantum chemistry packages. Despite that, several efforts have been done in order to tackle the singlet fission process entirely through the adiabatic point of view.

Morrison and Herbert have developed analytical expressions for the computation of nonadiabatic couplings<sup>212</sup> within a Frenkel-Davydov exciton model for the computation of excited states in molecular crystals and aggregates.<sup>326</sup> The same authors applied this methodology to investigate the role of vibronic couplings in tetracene,<sup>308</sup> identifying intramolecular modes with frequencies in near-resonance with the  $S_1/{}^1\text{TT}$  gap as being crucial for the internal conversion to the triplet-pair state achieved by tuning state energies, in agreement with electronic calculations in tetracene dimers.<sup>135</sup>

Sato and collaborators developed a theoretical method for the calculation and analysis of vibronic couplings based on the vibronic coupling density (VCD) concept.<sup>327</sup> In this approach, the derivatives of the electronic Hamiltonian are expressed in terms of electron densities and transition densities and a potential derivative  $v_i$ :

$$\frac{\partial H_{IJ}}{\partial Q_i} \Bigg|_{Q=0} = \int d\mathbf{r} (\rho_I(\mathbf{r}) - \rho_0(\mathbf{r})) v_i(\mathbf{r}) \quad (57)$$

$$\frac{\partial H_{IJ}}{\partial Q_i} \Bigg|_{Q=0} = \int d\mathbf{r} \rho_{IJ}(\mathbf{r}) v_i(\mathbf{r}) \quad (58)$$

$$v_i(\mathbf{r}) = \sum_\alpha \frac{\partial}{\partial Q_i} \left( \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \right) \Bigg|_{Q=0} \quad (59)$$

where  $\{Q_i\}$  are the vibrational coordinates,  $I$  and  $J$  correspond to electronic states,  $\rho_0$  and  $\rho_I$  are the ground and excited state densities,  $\rho_{IJ}$  is the interstate transition density, and the  $\alpha$  index runs over the  $N_\alpha$  nuclei of the system with  $Z_\alpha$  atomic numbers. Ito et al. applied the VCD approach to the study of excited state energies and electronic couplings in a tetracene dimer model identifying specific high and low-frequency vibrational modes to have potential impact in singlet fission.<sup>328</sup>

Krylov and co-workers have developed a simple approach to estimate nonadiabatic couplings based on the reduced one-particle transition density matrix between initial and final (adiabatic) states (eq 60).<sup>106</sup> Since the derivative coupling is a one-electron operator, it can only couple states that differ by no more than a single excitation. From such reasoning it follows that the norm of the one-particle transition density matrix (eq 61) is proportional to the nonadiabatic coupling and can be used as a measure for the magnitude of the interstate interaction,<sup>268</sup>

$$\gamma_{pq}^{IJ} = \langle \Psi_I | p^+ q | \Psi_J \rangle \quad (60)$$

$$\|\gamma\| = \sqrt{\sum_{pq} \gamma_{pq}^{IJ} \gamma_{pq}^{JI}} \quad (61)$$

where  $p^+$  and  $q$  are one-particle creation and annihilation operators. Interstate  $\|\gamma\|$  values between a pure LE (or FE) state and a pristine  ${}^1\text{TT}$  state (eq 18) is zero, while the mixing with CT or CR contributions in the  $S_1$  and  ${}^1\text{TT}$  adiabatic wave functions allows for nonzero nonadiabatic couplings,<sup>106</sup> in agreement with conclusions drawn from the analysis of electronic couplings within the diabatic picture. Despite the simplicity of the approach, it can be used to qualitatively evaluate derivative couplings between adiabatic states and in particular to efficiently identify trends in the coupling strength along structural rearrangements such as intra or intermolecular distortions, and it has been used to evaluate patterns in the derivative couplings in tetracene and pentacene dimers.<sup>106,181–183,192,195</sup>

## 6. SINGLET FISSION DYNAMICS

The vast majority of the early theoretical and computation investigations on singlet fission were devoted to the characterization of the electronic states involved, the search for suitable chromophores with the optimal energetics, the evaluation and optimization of electronic couplings, and the determination of potential singlet fission mechanisms. These studies were based on static calculations (i.e., with no explicit dependence with time), and, at most, they were employed to estimate singlet fission rates through different kinetic models parametrized with experimental and/or computed energies and couplings (as discussed in previous sections).

On the other hand, time-resolved spectroscopic measurements (i.e., delayed fluorescence,<sup>72,329–331</sup> transient absorption,<sup>32,33,49,244,264,332–336</sup> or time-resolved two-photon emission)<sup>153,264</sup> have led the experimental investigations on singlet

fission and have pushed for a much more complete understanding regarding the fission mechanism, the time scales involved, and the key parameters controlling singlet fission efficiency, such as chemical composition and topology, in a variety of organic materials.

The simulation of explicit time evolution of the singlet fission process remained basically unexplored until 2010,<sup>200</sup> when a variety of computational approaches typically used for the study of electron and energy transfer processes started to be applied to the singlet fission problem. These investigations help to rationalize experimental measurements and complement static electronic structure calculations and are very important in order to achieve a more detailed understanding of the overall photophysical reaction.

The modeling of the singlet fission dynamics can be attained by quantum dynamics approaches able to simulate exciton energy transfer (EET) processes. In general, these phenomena can be seen as the relaxation of an out of equilibrium multilevel system coupled to a bath (i.e., those degrees of freedom from the environment that interact with the system). In singlet fission, such a path corresponds to the relaxation just after photoexcitation that leads to the formation of two independent triplets. This section does not intend to cover the complete (very long) list of approaches for the description of the dynamics of nonadiabatic processes, not even those specially dedicated to the study of the energy transfer phenomena. It aims to give an organized set of methodologies applied to singlet fission and the main conclusions derived from the computational results obtained so far in the field.

### 6.1. Wave Function Formalism

The time-dependent Schrödinger equation (eq 13) can be numerically solved with several approximations, such as the multiconfigurational time-dependent Hartree (MCTDH),<sup>337</sup> the density matrix renormalization group (DMRG),<sup>338</sup> or through path-integral techniques.<sup>339–343</sup>

The MCTDH approach is able to propagate the wave packet of the nuclei on one or more electronic states with explicit (discretized) bath modes. Such treatment is limited to a few number of degrees of freedom, and it has been successfully applied to the singlet fission problem<sup>104,190,344,345</sup> by considering the propagation of selected vibrational modes on the PESs of the lowest electronic states of the system. Probably the first theoretical study where MCTDH was applied to the investigation of the singlet fission mechanism was published in 2015 by Tamura and collaborators.<sup>104</sup> The authors performed a nonadiabatic quantum dynamics analysis fully parametrized against first-principles calculations. The study combines DFT geometry optimization and frequency analysis, multireference second-order perturbation theory calculations with MCTDH to solve the dynamics of singlet fission in TIPS-pentacene and rubrene. The calculations go beyond the dimer model, including up to three chromophores from the crystal structure. Moreover, diabatic states are obtained from a diabatization procedure by mixing the computed adiabatic eigenstates. From their analysis, the authors concluded that singlet fission in TIPS-pentacene occurs through an avoided crossing and that resonances between  $S_1$  and  ${}^1\text{TT}$  states are mediated by intramolecular vibrations. Vibronic coherence is transferred through the mixings with CT states (i.e., superexchange). On the other hand, the thermally activated singlet fission in rubrene takes place in the vicinity of a conical intersection controlled by the strength of two-electron coupling (no superexchange).

Zheng et al. applied a multilayer version of MCTDH (ML-MCTDH) to study singlet fission in pentacene dimers using a three-state model.<sup>344</sup> Their study highlights the importance of the superexchange mechanism in pentacene, in agreement with Redfield results.<sup>202</sup> Moreover, their results indicate that vibrational modes in resonance with the  $S_1 \rightarrow {}^1\text{TT}$  gap (0.17–0.20 eV) have a major impact in the singlet fission of pentacene and are responsible for the ultrafast interstate transition as suggested by previous electronic structure calculations,<sup>135</sup> while lower frequency modes have a much weaker role. Zeng and Goel combined diabatization of sophisticated electronic structure calculations (general multiconfigurational quasidegenerate perturbation theory)<sup>346</sup> with MCTDH to design small molecular covalent dimers potentially able to undergo singlet fission.<sup>190,345</sup> Very recently, Monahan et al., using MCTDH simulations in conjunction with time-resolved photoemission and transient absorption spectroscopies, concluded that the quantum coherent and incoherent mechanisms for the formation of the triplet-pair state coexist in crystalline hexacene,<sup>347</sup> which could explain the existence of different interpretations (coherent vs incoherent) for the singlet fission mechanism in crystalline acenes. The possibility of simultaneous coherent and incoherent paths has also been proposed for singlet fission in rubrene single crystals.<sup>348</sup>

Time-propagation of electronic states can also be explored with the use of DMRG wave functions.<sup>338,349–351</sup> Yao treated both local (intramolecular) and nonlocal (intermolecular) vibrational modes quantum-mechanically in the frame of time-dependent DMRG to study singlet fission dynamics in tetracene and TIPS-pentacene.<sup>352</sup> In agreement with other investigations, the study concluded that CT states couple to nonlocal phonons, which accelerate the  $S_1 \rightarrow {}^1\text{TT}$  transition by enhancing the mediated mechanism (superexchange) and promoting ultrafast singlet fission. The obtained results suggest that nonlocal couplings might be enhanced by exciton delocalization, thus being another factor contributing to increasing singlet fission yields.

**6.1.1. Stochastic Dynamics in Hilbert Space.** The dynamics of open quantum systems can be treated from a viewpoint of a stochastic process in Hilbert space. Within this frame, stochastic Schrödinger equations (SSE) have been derived to describe time evolution in quantum mechanics. A special case of SSE is the time-dependent wavepacket diffusion method (TDWPD).<sup>353,354</sup> The TDWPD is a stochastic approach where the effect of electron–phonon interactions is incorporated by random fluctuations obtained from spectral density functions, which act on the site energies and electronic couplings between sites. The TDWPD method can be seen as a sophistication of the Haken-Strobl-Reineker (HSR) model,<sup>355–357</sup> where the vibrational motions are considered classically and the system motion as quantum trajectories where the noise from the environment acts continuously at each time step of the evolution. The TDWPD approach has been used to model singlet fission dynamics in organic aggregates using a 1D model<sup>358</sup> and to explore the impact of exciton migration through the aggregates. The results point toward an increase of fission rates with aggregation length, while electronic couplings between different  ${}^1\text{TT}$  states decrease the singlet fission kinetics. The study also highlights the importance of CT mediated mechanisms and the interferences between the direct and mediated paths.

## 6.2. Generalized Quantum Master Equation

A variety of methodologies considering the quantum treatment of the environment degrees of freedom (bath) are based on different approximations to the Liouville-von Neumann quantum master equation (eq 62),

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar} [H, \rho(t)] \quad (62)$$

where  $\rho(t)$  is the total time-dependent density matrix and  $H$  is the system-bath Hamiltonian. Formally exact solutions to eq 62 have been developed in order to describe the time-evolution of the relevant part of the system by means of reduced density matrices (RDMs). This is the case of the Nakajima-Zwanzig equation<sup>359,360</sup> or the hierarchical equations of motion (HEOM).<sup>361,362</sup> But in practice, such solutions are not affordable (unless cases with only very few degrees of freedom), and different approximations are commonly applied. Approximations to eq 62 are ultimately perturbative in nature. On one hand, there are models that treat the coupling between electronic and bath degrees of freedom formally in an exact manner, while treating electronic couplings perturbatively (NIBA like approaches). On the other hand, Redfield theories and related methods treat the electronic couplings exactly, and the system-bath interaction as a perturbation.

In general, approaches to the Liouville-von Neumann quantum master equation can either take into account nonequilibrium phonons (non-Markovian dynamics) or consider that the bath modes remain in equilibrium (Markov approximation).<sup>363,364</sup> As a general prescription, if the bath relaxation time is shorter than the studied process, the Markovian dynamics can be safely applied. On the other hand, if the bath relaxes within the same (or larger) time scale as the system, memory effects might have a sensible impact on the system dynamics and the non-Markovian form should be used instead. The suitability of the Markov approximation has been discussed within the frame of singlet fission by various authors.

The application of dynamic models based on the quantum master equation to the study of singlet fission has produced already a fare amount of results, which have helped to reinforce some of the conclusions already drawn in static calculations, but it has also brought into light new important aspects of the singlet fission mechanism. When applied to the singlet fission problem, in addition to the study of exciton dynamics in specific systems, in many cases pentacene, these methods have been employed to explore different regimes, many related to the energies and interstate couplings between  $S_1$ ,  $^1\text{TT}$ , and CT. This has allowed one to extract and highlight rather general conclusions upon the approximations introduced by the quantum dynamics model (e.g., three vs five state models, markovian or nonmarkovian approach, etc.).

In 2010, Greyson et al.<sup>200</sup> employed (phenomenological) density matrix theory in the limit of fast coherent transfer to explore the singlet fission dynamics in molecular coupled pairs. A very similar approach was later used to investigate the singlet fission coherent dynamics in crystal tetracene.<sup>264</sup> The study by Greyson et al. pointed toward the idea that the energetics of electronic states has a much larger impact on the singlet fission efficiencies than the electronic couplings (obtained in their study as electron transfer matrix elements). These results help to justify those efforts trying to find molecular chromophores with optimal singlet-triplet energetics as the main criteria in

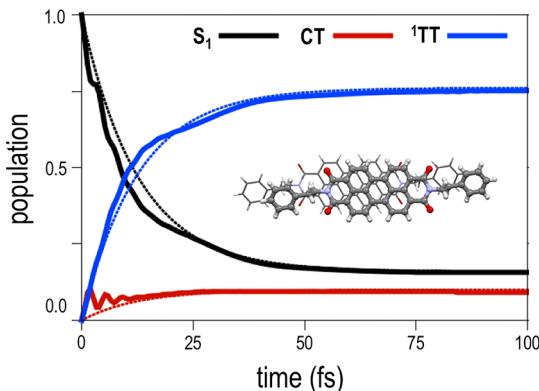
search of good singlet fission materials. The authors also concluded that within the coherent regime, high fission yields are achieved for small free-energy differences ( $\Delta G \sim 0$ ) between the single exciton ( $S_1$ ) and the  $^1\text{TT}$  state, hence large exothermicity is not desired. Having the CT state energetically not too high with respect to  $S_1$  and  $^1\text{TT}$  is also an important factor for the formation of the triplet-pair, but to a lesser extent than near-degeneracy. The authors also acknowledged that dynamical effects might have a large impact in singlet fission efficiencies. Since high symmetry systems present interference effects that lead to the effective cancelation of  $S_1/\text{CT}$  and  $\text{CT}/^1\text{TT}$  electronic couplings, the activation of symmetry breaking modes of the environment might reduce interference, increasing singlet fission yields (although the authors did not include dephasing in their model, they suggested that it could be another source to diminish interference).

The  $S_1/^1\text{TT}$  near-degeneracy rule was later reinforced by Teichen and Eaves.<sup>201</sup> Their study was based on a NIBA-like approach with exact treatment of the bath and propagation of the reduced density matrix of a three state model coupled to environment vibrations. The obtained results evidenced how low-frequency solvent modes can substantially impact the singlet fission yields, either facilitating or hindering the formation of the  $^1\text{TT}$  state. Non-Markovian effects related to these modes might be important within the initial few picoseconds after photoexcitation, questioning the use of the golden rule.

The suitability of NIBA-like approaches for the study of singlet fission has been put in doubt<sup>294</sup> due to the magnitude of the electronic couplings with respect to the reorganization energies in typical singlet fission systems. The perturbative treatment of electronic degrees of freedom seems inappropriate, since it cannot describe the CT-mediated singlet fission path. To overcome such limitations, Berkelbach et al. described a quantum dynamics model based on the Redfield approximation to the Liouville-von Neumann expression (eq 62) and applied their formulation to the exciton dynamics in dimers, clusters, and molecular crystals in a series of papers dedicated to singlet fission.<sup>107,202,294</sup> The validity of their model was tested against HEOM and used to explore memory effects by comparing between Markovian (time-local) and non-Markovian forms. The obtained results seem to justify the perturbative treatment of electronic-vibrational coupling in the study of singlet fission (at least for pentacene). The application of the Redfield equation to the study of singlet fission in pentacene dimers describes the role of CT (virtual) states in terms of the superexchange concept in the diabatic picture.<sup>202</sup> This study helped to clarify how singlet fission can be mediated by energetically high CT states. Later on, the study of Fujihashi and Ishizaki on the singlet fission dynamics of pentacene dimers concluded that the mixing of CT contributions to the  $S_1$  and  $^1\text{TT}$  states is rather robust to fluctuations in the energy of CT states.<sup>365</sup> Despite that singlet fission in pentacene dimers and crystal pentacene exhibit similar time scales, these two cases show important qualitative differences.<sup>107</sup> In particular, in the bulk, the adiabatic  $S_1$  state is strongly mixed to CT contributions, which are energetically lower than in the pentacene dimer. Eventually, the relative orientation and distance between chromophores in the crystal will dictate the CT mixing and the singlet fission mechanism to take place, favoring one or two-electron Coulomb interactions toward the  $^1\text{TT}$  state. The Redfield model was later extended to take into account multiphonon relaxation processes. This approach was

applied to the study of singlet fission in crystalline hexacene in combination with transient absorption measurements.<sup>273</sup> The study revealed a fission time scale in hexacene of 530 fs, much faster than in tetracene but slower than in pentacene. Despite larger exothermicity in hexacene than in pentacene, the lack of available high-energy phonons along the relaxation process requires the assistance of multiple modes, which slows down singlet fission in hexacene.

The Markovian form of Redfield theory was applied by Mirjani et al. to further understand the role of CT and quantum interference in molecular dimers and aggregates.<sup>366</sup> The study discusses the dependence of different electronic couplings on displacements along the stacking disposition of molecular dimers of PDI, pentacene, and 1,3-diphenylisobenzofuran, and how it can sensibly modify the singlet fission dynamics suggesting optimal orientations to promote the formation of the <sup>1</sup>TT state. The differences between different systems are controlled by the presence of CT states and their relative energies with respect to the  $S_1$  state, in agreement with the superexchange idea,<sup>202</sup> with no effective population of CT states (Figure 8). The study also discusses how quantum



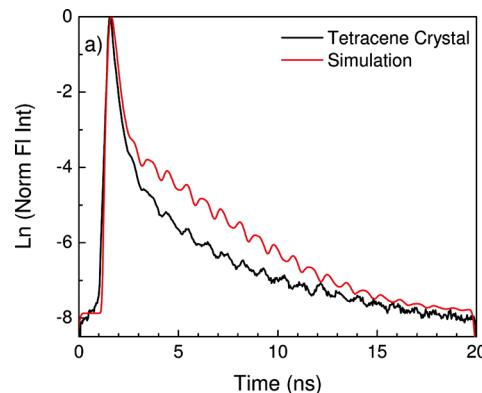
**Figure 8.** Population of  $S_1$  (black), <sup>1</sup>TT (blue), and CT (red) states for a PDI derivative (inset) obtained with the Redfield approach. Figure adapted from ref 366. Copyright 2014 American Chemical Society.

interferences between direct and mediated paths might influence the singlet fission dynamics, which might eventually increase or decrease the fission rates. In a follow-up study, Renaud and Grozema explored the role of intra (Holstein) and intermolecular (Peierls) vibrations in the singlet fission dynamics of PDI crystals.<sup>310</sup> The results obtained with a non-Markovian quantum jump technique within Redfield theory identified intermolecular vibrations between PDI molecules with a frequency close to the  $S_1$ /<sup>1</sup>TT energy gap as potential catalysts for the interstate transition by modifying the magnitude of the two-electron couplings.

The Holstein couplings in pentacene dimers have been further investigated by means of the second-order time-convolutionless (TCL) approach to the quantum master equation and by the use of relative relaxation factors as analysis tool.<sup>367</sup> The obtained results also point toward the idea that the mixing of CT contributions in  $S_1$  and <sup>1</sup>TT states is crucial for fast singlet fission in these systems. In line with previous studies, the authors conclude that the energy matching condition speeds up triplet-pair formation, but it might eventually decrease the singlet fission yield. Moreover, intense vibronic coupling in CT compensates for low mixings due to

large energy gaps, allowing for simultaneous fast rates and high <sup>1</sup>TT yields. The importance of the coupling of electronic states to vibrations of the nuclei in order to connect  $S_1$  and <sup>1</sup>TT states is in agreement with coherent two-dimensional ultrafast spectroscopy in pentacene derivatives.<sup>307</sup>

A density matrix propagation model has also been employed to study the origin of the quantum beating in delayed fluorescence in tetracene (Figure 9).<sup>72,155</sup>



**Figure 9.** Time-resolved photoluminescence of a tetracene single crystal displaying quantum beats in the delayed fluorescence (black). In red simulated signal calculated using a density matrix approach. Reproduced from ref 72. Copyright 2012 American Chemical Society.

Quantum beating results from the recombination of coherent geminate triplet-pairs, and it is a proof of the formation of the triplet-pair state. The employed model identifies the quantum beat frequencies in crystalline and polycrystalline tetracene as the energy differences between the three triplet-triplet states with singlet character:  $|xx\rangle$ ,  $|yy\rangle$ , and  $|zz\rangle$  in eq 19. The beating profile is temperature-dependent, and the progressive disappearance of the beats in the fluorescence spectrum at low temperatures is consistent with the decrease of singlet fission rate.

### 6.3. Quantum-Classical Nonadiabatic Dynamics

The dynamics of excited energy transfer processes, such as singlet fission, can be studied by mixed quantum-classical approaches,<sup>368–370</sup> where electrons are treated quantum mechanically, while the fluctuations of the atomistic structure are treated classically. The trajectory-based solutions of the nuclear dynamics can be coupled to electronic structure calculations without the need to limit the atomic motions to a rather small number of relevant degrees of freedom. Moreover, quantum-classical hybrid approaches proportionate an atomistic description of the dynamics of the system and are able to deal with fast bath dynamics. Many of these methods use the idea of trajectories hopping between different electronic potential energy surfaces<sup>371–378</sup> and are based on the original trajectory surface hopping (TSH) method developed by Tully.<sup>379,380</sup>

The first computational investigation of singlet fission relying on nonadiabatic quantum molecular dynamics (NAQMD)<sup>381</sup> coupled classical nuclear motion with TDDFT calculations and the surface hopping approach<sup>379</sup> and was dedicated to the study of singlet fission in amorphous 5,12-diphenyltetracene (DPT).<sup>382</sup> The study employed NAQMD results as input to kinetic Monte Carlo (KMC)<sup>383</sup> simulations. The obtained results helped to confirm experimental investigations,<sup>335</sup>

suggesting that singlet fission in amorphous DPT occurs mainly in a few optimally oriented DPT molecular pairs (i.e., fission hotspots) and provided precise geometrical description of efficient DPT dimers.

A rather recently developed surface hopping technique [i.e., the self-consistent fewest switches surface hopping (SC-FSSH)],<sup>375</sup> combined with electronic structure calculations has also been employed to explore the optimal intermolecular packing in pentacene using molecular dimers as model systems for singlet fission.<sup>278</sup> In particular, the study focused on the impact of molecular (Holstein) vibrations, corresponding to the electron–phonon coupling to carbon–carbon stretching modes. The obtained results point toward slip-stacked dimer configurations favoring high singlet fission yields, in agreement with ultrafast pump–probe experiments<sup>242</sup> and electronic structure calculations.<sup>279</sup> Moreover, the study indicates that one should be cautious when using symmetry-based arguments to determine nonvanishing couplings from (static) electronic structure calculations to analyze singlet fission. Although these might be very informative, the strict symmetry rules can be sensibly relaxed or even discarded when thermal fluctuations are taken into consideration. The study also concludes that the instantaneous formation of the triplet–triplet pair upon photoexcitation maximizes singlet fission efficiency by simultaneously favoring high triplet yields and rates. A similar computational methodology has been applied to the ab initio study of nonadiabatic dynamics of singlet fission in pentacene coupled to the electron transfer process at the pentacene/C<sub>60</sub> interface.<sup>384</sup>

#### 6.4. Quasi-Classical Dynamics

Another manner to approximate nonadiabatic dynamics is the use of quasi-classical (QC) models to classical molecular dynamics simulations.<sup>385</sup> Several versions derived from the initial quasi-classical model have emerged, although probably the most standard methods employ window functions (“Gaussian binning”) in order to recover quantum state information from classical models.<sup>386</sup> One of the QC approaches that makes use of window functions is the symmetrical quasi-classical (SQC) nonadiabatic molecular dynamics approach,<sup>387</sup> which has been repeatedly applied to explore general aspects of the singlet fission dynamics.<sup>309,388,389</sup>

The use of explicit atomic and electronic degrees of freedom, and the exact treatment of the electronic-nuclear coupling,<sup>390</sup> has allowed identifying potential interferences between the direct and mediated pathways.<sup>388</sup> Despite the generally rather weak direct (two-electron) S<sub>1</sub>/<sup>1</sup>T<sub>1</sub> coupling, cooperative effects with the mediated coupling can eventually play a significant role in singlet fission. Simulations of the singlet fission dynamics in molecular dimer models suggest that coherences between the two mechanisms could notably modify the time evolution at early stages of the reaction and impact the overall decay rates. The SCQ method has also been used to determine the effect of electronic energies, electronic couplings, and electronic-phonon interactions, as well as bath modeling in singlet fission.<sup>309,389</sup> These studies have highlighted the critical role of reorganization energy, and assert that singlet fission dynamics exhibits almost no dependence with temperature for high-energy phonons, while it is temperature-dependent for low frequency modes.

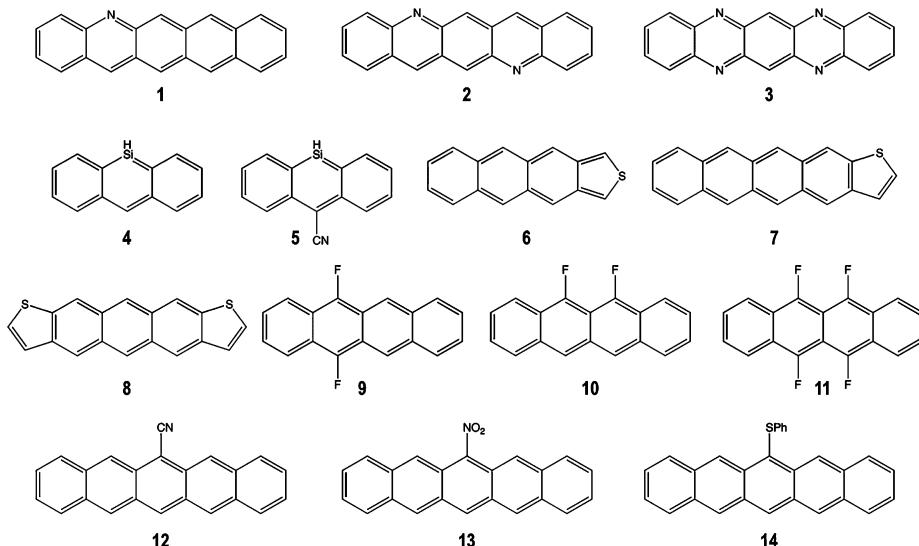
## 7. SINGLET FISSION CHROMOPHORES

The precise characterization of individual chromophores is of vital importance since these are the building blocks of the multichromophoric system. Electronic states' properties of the monomers, in particular low-lying excited singlets and triplets, will ultimately define, to a large extent, the singlet fission capabilities of the material. Therefore, accurate estimation of absolute and relative excitation energies is fundamental in the search for new compounds with improved fission properties and has become the first step in the computational study of the singlet fission mechanism. An excellent example of such computational screening is the pioneering work by Michl et al. in 2006,<sup>25</sup> in which the authors proportionated a detailed rationale for the molecular design of singlet fission compounds. Those guidelines have inspired many theoretical and computational subsequent investigations. On the basis of the main energetic requirements to be fulfilled by a singlet fission sensitizer discussed in section 2.2 [i.e., E(T<sub>2</sub>), E(S<sub>1</sub>) ≥ 2E(T<sub>1</sub>)], two possible paths for the design of molecular candidates have been proposed: (i) closed shell molecules with a relatively low-lying S<sub>1</sub> state (compatible with optimal light harvesting properties<sup>23</sup>) and strong electronic exchange interaction between the HOMO and LUMO in order to open the S<sub>1</sub>–T<sub>1</sub> gap, typically much smaller than the S<sub>1</sub>–S<sub>0</sub> energy separation. (ii) Structurally distorted diradicals with interaction between the two radical centers (diradicaloids) in order to break the degeneracy or near-degeneracy between T<sub>1</sub> and S<sub>0</sub> by lifting the energy of T<sub>1</sub> with respect of the ground state.

These two approaches have been used to identify two families of molecular structures as singlet fission sensitizers: (i) large alternant hydrocarbons and (ii) diradicaloids, respectively. These two families of compounds are not disjointed. Indeed, this is the situation in pentacene, the archetype singlet fission chromophore, for which the diradical character (diradicaloid) has been computationally assessed in numerous occasions.<sup>391–396</sup> In the following, I will discuss, mainly from a theoretical and computational point of view, the main advances in the search of the two types of chromophores for their use in singlet fission.

### 7.1. Large Alternant Hydrocarbons

The two conditions defining the first type of molecules can be potentially fulfilled in large alternant hydrocarbons,<sup>25</sup> since conjugated hydrocarbons with no odd-membered rings exhibit large HOMO/LUMO overlap (large exchange interaction), and the increase of conjugation length in  $\pi$ -electron systems stabilizes the S<sub>1</sub> state. It is important to note that this strategy completely disregards the energy condition related to the accessibility to the T<sub>2</sub> state. Historically, this class of chromophores has constituted the large majority of systems initially known to experience singlet fission. As such, much effort has been focused in their characterization, and they have been used as the backbone in the design of new compounds through chemical substitution. In particular, several computational studies have tried to expand the list of singlet fission compounds by modifications of tetracene and pentacene either by heteroatom replacement of some of the carbon atoms<sup>397,398</sup> or by chemical functionalization.<sup>399,400</sup> To some extent, these investigations try to identify chromophores with proper energy-matching conditions at the chromophore level by tuning the relative energies of the low-lying singlets and triplets. But maybe even more importantly, these efforts can also tackle other issues not directly related to the fission mechanism but



**Figure 10.** Molecular structures of heteroacenes and functionalized acenes proposed as chromophore candidates for singlet fission.

that might critically limit the singlet fission capabilities. Concretely, chemical substitutions might alleviate molecular degradation under molecular oxygen exposure,<sup>401–405</sup> increase the overall chemical stability<sup>406</sup> or photostability,<sup>407</sup> or modify the solubility of the parent structure.

**7.1.1. Examples.** Next, I shortly present several examples of the effect of chemical substitution in alternant hydrocarbons, more specifically in acenes, regarding their capabilities as singlet fission sensitizers. I limit the discussion to only some of the most recent theoretically proposed and computationally investigated systems as shown in Figure 10.

**N-Heteroacenes.** The potential use of N-heteroacenes in optoelectronic applications has recently attracted some attention,<sup>408–411</sup> and they have been also investigated for their potential suitability as singlet fission chromophores.<sup>397</sup> Nitrogen substitution in pentacene stabilizes the HOMO and LUMO energies with respect to the unsubstituted parent acene, which can be related to the electron-withdrawing capacity of nitrogen.<sup>410</sup> Energy lowering of frontier orbitals could improve the chemical stability of these molecules<sup>406</sup> and decreases the singlet–triplet gap, which might reduce energy losses along the fission process. Computational results reveal how the position and the number of nitrogen atoms can be used to tune the electronic properties of nitrogen-containing heteroacenes (**1–3**).

**Si-Heteroacenes.** Datta et al. realized that silicon substitution in oligoacenes reduces more significantly the energy gap from the ground state singlet to  $T_1$  than to the lowest excited singlet. As a result, silicon substitution induces a shift within the acenes series for which the optimal energy matching condition is met [i.e., from the five linearly fused benzene rings (pentacene) in pristine acenes toward smaller systems in Si-heteroacenes].<sup>398</sup> Concretely, electronic structure calculations predict 9-silaanthracene (**4**) as having the best relative state energies along the monosilicon substituted linear acenes. The singlet–triplet energy gap in **4** was further tuned through functionalization with different electron withdrawing groups. Computational results found that in **5**, the  $T_1$  state lies exactly at half of the  $S_1$  energy. The study of **5** was further extended to the simulation of crystal structure by means of periodic DFT calculations. The computation of electronic couplings in molecular dimers in the crystal predicts

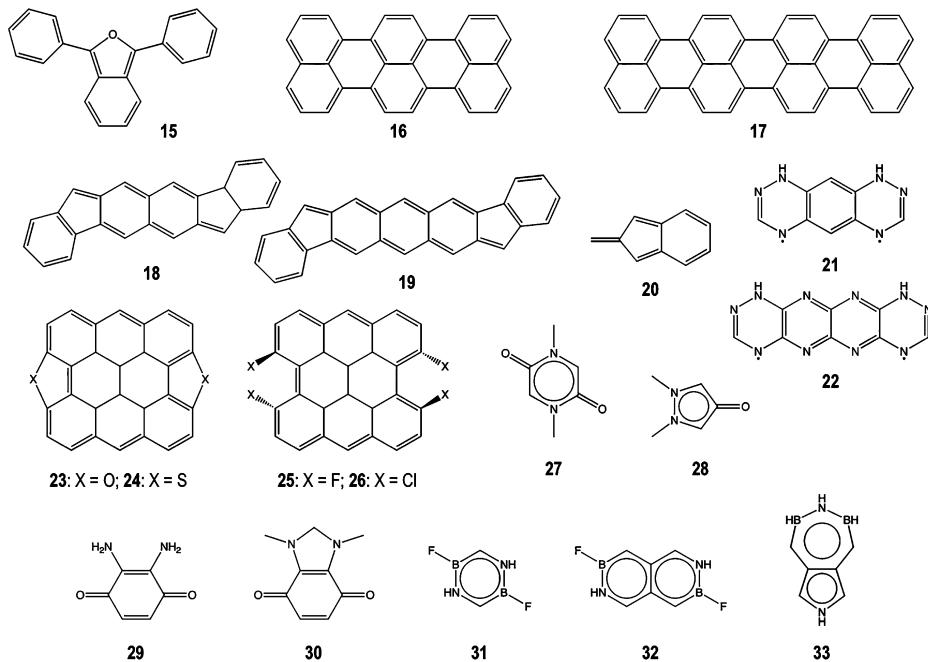
large fission efficiencies. As far as I know, these results have not been confirmed experimentally.

**Acene-Thiophene.** The unique electronic and optical properties of the thiophene ring, which is one of the most employed  $\pi$ -conjugated building blocks in the field of organic photovoltaics, has contributed enormously to the development of high-performance organic optoelectronic devices.<sup>412</sup> These special characteristics have motivated studying the impact of replacing a six-membered ring in tetracene and pentacene by the thiophene moiety considering different substitution patterns (**6–8**).<sup>397</sup> The electronic properties of these systems vary with the position of the thiophene within the molecule, the number of thiophene rings, and the type of connection between thiophene and benzene units. The different participation of the sulfur atomic orbitals in the frontier molecular orbitals and the delocalization of the sulfur electron pairs in the conjugated system<sup>413</sup> depends on the type of substitution, and can be used to rationally tune HOMO–LUMO gaps, and  $T_1$  and  $S_1$  energies in these thiophene-substituted molecules. Analysis of the computed relative energies combined with stability and solubility considerations<sup>402</sup> indicate compound **7** as a good candidate for singlet fission.

**Functionalized Acenes.** Li et al. investigated the impact of mono and multifunctionalization on the fission energies and molecular stability of tetracene<sup>399</sup> and pentacene (**9–14**).<sup>400</sup> On the basis of the energy levels of frontier molecular orbitals, the authors concluded that substitution with electron-withdrawing groups might improve the stability toward oxidation. On the contrary, the presence of electron-donating moieties is detrimental for their stability. The evaluation of obtained singlet fission activation energies suggests difluorotetracenes (**9** and **10**), tetrafluorotetracene (**11**), and **12**, **13**, and **14** substitutions of pentacene as promising chromophores.

## 7.2. Diradicaloids

Recently, the search for molecular sensitizers following the diradicaloid strategy has become an intense field of research in singlet fission. The potentially unlimited diversity of diradicaloid molecules might eventually crystallize in the design of chromophores with the optimal energetics. Such expectations have motivated numerous studies of molecular diradicaloid species in the frame of singlet fission (Figure



**Figure 11.** Structures of molecular diradicaloids proposed as chromophore candidates for singlet fission.

11). In many instances, computational design has led this research, and even in some cases promising computational results have motivated the synthesis and experimental characterization of molecular diradicaloids to be tested for singlet fission, such as the case of 1,3-diphenylisobenzofuran (15).<sup>414–417</sup>

#### 7.2.1. Diradical Character in Singlet Fission.

Since 2006, the computational search for singlet fission molecular sensitizers has been, in many cases, related to the characterization of its diradical character.<sup>25</sup> Nakano et al. have explored in detail the connections between diradical character and singlet fission by analyzing quantitative correlations between the ground state open-shell nature of molecules and their fission efficiency.<sup>418</sup> Diradical (or biradical) refers to molecular species having two unpaired electrons (i.e., two independent or near-independent electrons).<sup>419</sup> The weak interaction of the two radicals results in a diradical-like species (diradicaloid), where the degeneracy between “singly occupied orbitals” is lifted resulting in a partial diradical character.

Due to their inherent complexity and their potential use in different applications, such as in singlet fission, diradical (and diradicaloid) organic molecules have attracted a lot of interest both from the experimental and theoretical chemistry community.<sup>420,421</sup> Diradicals are typically rather unstable with a large tendency to react with the environment.<sup>422</sup> From a theoretical point of view, they present a more complex electronic structure than the typical closed-shell configuration of many organic molecules. In particular, the electronic structure characterization of diradicals is a challenge for many quantum chemistry models and deserves special treatment.

The computational quantification of the diradical and poly radical character of electronic states is typically based on the analysis of occupation numbers of natural orbitals. This is the case of the use of the spin-projected unrestricted Hartree–Fock (PUHF) method, for which the multiple diradical character ( $y_i$ ) are defined as<sup>423</sup>

$$\gamma_i = 1 - \frac{2T_i}{1 + T_i^2} \quad (63)$$

where index  $i$  refers to the multiple diradical degree [i.e., diradical ( $y_0$ ), tetraradical ( $y_1$ ), etc.]. The  $T_i$  terms can be expressed as a function of the occupation numbers of the UHF natural orbitals ( $n_i$ ):

$$T_i = \frac{n_{\text{HONO}-i} - n_{\text{LUNO}+i}}{2} \quad (64)$$

The diradical character  $y_0$  was correlated to relative energies between the lowest triplet and singlet states<sup>424</sup> and then expanded to the study of singlet fission using  $y_0$  and  $y_1$  as indicators. On the basis of the singlet fission energy matching conditions, the analysis of the two indices obtained for typical singlet fission chromophores indicates that some diradical character is required for efficient singlet fission ( $y_0 > 0.1$ ), while tetraradicals ( $y_0 \sim y_1$ ) are not adequate. The fission efficiency decreases for large values of  $y_0$ , since singlet fission becomes too exothermic. In other words, diradicaloids might be good for singlet fission, while perfect diradicals are not.

The two site model with two electrons in two orbitals using the valence CI (VCI) method<sup>425,426</sup> has been used as an alternative to PUHF in the singlet fission context. Within the VCI scheme, the diradical character  $y_0$  can be expressed as

$$\gamma_0 = 1 - \frac{1}{\sqrt{1 + \left(\frac{U}{4t}\right)^2}} \quad (65)$$

where  $U$  is the on-site Coulomb interaction and corresponds to  $E(S_1) - E(T_1)$ , and  $t$  is a transfer integral related to the mobility of an electron between sites. In this model, the transition energies to  $T_1$  and  $S_1$  states can be expressed as

$$E(S_1) = \frac{U}{2} \left( \frac{1}{\sqrt{1 - (1 - \gamma_0)^2}} + 1 \right) - 2K_{ab} \quad (66)$$

$$E(T_1) = \frac{U}{2} \left( \frac{1}{\sqrt{1 - (1 - \gamma_0)^2}} - 1 \right) - 2K_{ab} \quad (67)$$

where  $K_{ab}$  is the intersite exchange interaction. Eqs 66 and 67 clearly expose the relationship between the diradical character and the singlet fission energy requirements, since the  $2E(T_1) - E(S_1) \leq 0$  condition can now be expressed in terms of  $\gamma_0$ .

$$\frac{U}{2} \left( \frac{1}{\sqrt{1 - (1 - \gamma_0)^2}} - 3 \right) - 2K_{ab} \leq 0 \quad (68)$$

Evaluation of eq 68 for different  $U/K_{ab}$  ratios agrees with the idea that weak diradical character is necessary for efficient singlet fission.<sup>427</sup>

**7.2.2. Examples.** The analysis of the diradical ( $\gamma_0$ ) and tetraradical ( $\gamma_1$ ) indices has been repeatedly applied to the characterization of different families of compounds potentially interesting for singlet fission.<sup>418,428</sup> Nakano et al. have performed a series of electronic structure calculations using a variety of methods (TDDFT with a tuned range-separation parameter, SF-DFT, CASSCF, and RASPT2) to estimate the energy level conditions in antiaromatic ( $4n$   $\pi$ -electrons) condensed-ring  $\pi$ -conjugated systems,<sup>429</sup> oligorylenes,<sup>430</sup> phenacenes, acenes and isobenzofluvenes,<sup>427</sup> heteroacenes,<sup>431</sup> and bisanthene derivatives.<sup>432</sup> Moreover, analysis of the  $\gamma_0$  and  $\gamma_1$  indices for all these systems reinforces the idea of the suitability of intermediate diradicals with no tetraradical character as potentially good singlet fission sensitizers. The obtained computational results for antiaromatic and short oligorylenes identified terrylene (**16**) and quaterrylene (**17**), and indo-fluorene-like molecules **18** and **19**, as having the appropriate energetics for singlet fission. Interestingly, the predicted suitability of **16** was later experimentally confirmed in crystals of terrylene derivatives.<sup>241</sup> The combination of SF-DFT calculations with the two-site approach for  $\gamma_0$  has been applied to the systematic study of phenacenes, acenes, and isobenzofluvenes. The results indicate that, similar to tetracene and pentacene, isobenzofluvene **20** holds the proper energetics and diradical characteristics for singlet fission. Motivated by the singlet–triplet relative energies and diradical character exhibited by non-Kekulé heteroacenes,<sup>433–437</sup> Ito and Nakano explored a series of N-heteroacenes derived from anthracene and tetracene<sup>431</sup> and predicted **21** and **22** to exhibit exothermic fission. The bisanthene molecule is a diradicaloid,<sup>438</sup> but its diradical character appears to be too large for singlet fission applications. Computational analysis indicates how chemical substitution can be employed to decrease its diradical character and meet the energy matching conditions.<sup>432</sup> In this sense, two possible strategies were proposed as successful paths for the design of promising singlet fission chromophores: aromatic ring attachment (**23** and **24**) and twisting of the bisanthene core (**25** and **26**).

One of the strategies to devise good singlet fission molecular candidates has been based on the theoretical and computational design of small diradicaloid chromophores.<sup>300,439,440</sup> One of the main advantages of small diradicaloids is the fact that they can be chemically and structurally very distinct with respect to the typical singlet fission chromophores, hence they have the potential to expand the set of singlet fission materials beyond the chemical substitution of tetracene or pentacene. Compared to larger molecules, small chromophores might be easier to

synthesize and characterize. Additionally, from the computational point of view, these molecules can be treated with highly accurate methods, allowing for the fine prediction of the relative energies of low-lying excited singlet and triplet states.

The use of the synergistic effect through the combined action of electron-releasing and an electron-withdrawing substituents (i.e., the captodative effect)<sup>441</sup> is a well-known route for the stabilization of radical centers, which can facilitate the presence of two unpaired electrons in small molecules. This strategy was used for the first time in the frame of singlet fission by Michl et al. in the design of 5-membered and 6-membered diradicaloid heterocycles with an amine as the donor group and a carbonyl as the acceptor.<sup>300</sup> In their study, the authors took advantage of the manageable size of the chromophores to investigate with high accuracy vertical and adiabatic transitions to the low-lying singlet and triplet states. On the basis of the  $S_1$ ,  $T_1$ , and  $T_2$  relative energies the study identified two molecules (**27** and **28**) as promising singlet fission sensitizers. The suitability of **27** has been recently investigated beyond the analysis of the properties for the isolated chromophore with special attention to the evaluation of electronic couplings.<sup>301</sup> Computational results based on the simulation of the crystal structure using a periodic DFT approach with dispersion interaction correction<sup>442</sup> and the calculation of diabatic couplings with a nonorthogonal CI methodology<sup>103,443,444</sup> and a cluster (dimer) model indicate weak interaction of Frenkel excitons with CT configurations, which act as virtual states mediating the  $S_1 \rightarrow {}^1TT$  internal conversion.

In the search for stable diradicaloids appropriate for photovoltaic applications<sup>26,43</sup> (i.e., with high extinction coefficients approximately at 2.2 eV),<sup>23</sup> Michl and collaborators theoretically designed and computationally explored a set of 14 small mono and bicyclic planar heterocycles.<sup>440</sup> In their study, the authors developed a smart stepwise scheme for the rational design of captodatively stabilized diradicaloids starting from an ideal diradical and making use of the Hückel model, long-range corrected (LRC) TDDFT calculations and CASPT2 vertical and adiabatic excitation energies. Analysis of the relative excited state energies identify a diaminoquinone molecule (**29**) as the most promising one in their study, although the authors anticipated practical difficulties due to the potential presence of hydrogen bonds in aggregates or the twist of the amino group in the excited state. Alternatively, the structure of molecule **30**, although the computed energy for its lowest triplet state is too low for photovoltaics, does not present the potential practical inconveniences of **29** and might be preferred.

Zeng et al. followed a similar strategy based on the perturbation of small diradicals via heteroatom substitution to design new singlet fission chromophores.<sup>439</sup> The study explores the effect of mono and doubly BN-substitution in  $\pi$ -conjugated rings, which induces diradical captodative stabilization due to the electron donor and acceptor character of nitrogen and boron atoms, respectively. The results obtained from highly accurate MRMP calculations were used to evaluate the singlet fission energy criteria, light harvesting capabilities related to the Franck–Condon vertical transition energy and oscillator strengths, chemical stability, and the presence of potential competing deactivation pathways for a rather large set of chromophores. The study proposed three chromophores (**31**, **32**, and **33**) as potential candidates to be experimentally tested as singlet fission compounds in its crystalline form.

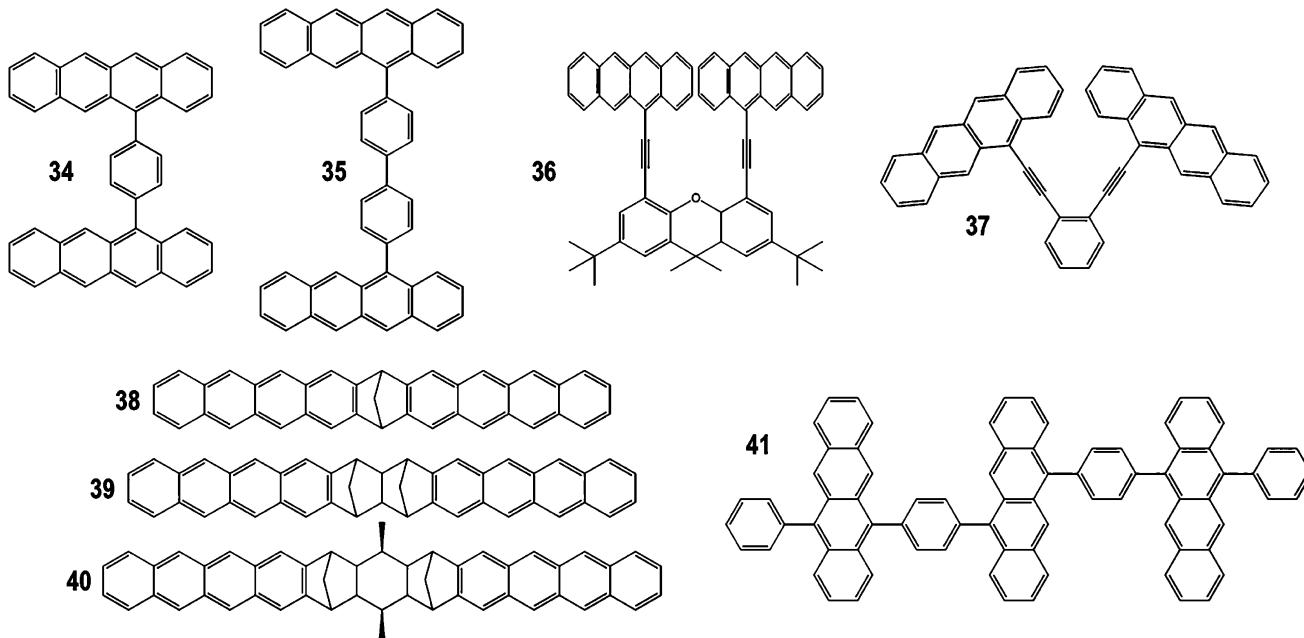


Figure 12. Structures of singlet fission covalent tetracene dimers.

## 8. SINGLET FISSION MATERIALS

### 8.1. Covalent Dimers

The covalent assembly of two chromophores is the smallest system potentially able to undergo singlet fission. Molecular crystals such as crystalline tetracene and pentacene are rather complex materials with many defect states that may interfere with the exciton decay via singlet fission.<sup>137,445</sup> On the contrary, covalent dimers are much simpler systems, which allow much control on interchromophore orientation and interaction. Moreover, they can be used to explore the intricacies of singlet fission mechanism and dynamics in great detail. The relative orientation and distance between monomers in covalent dimers can be controlled more easily, almost at will, than in molecular crystals or thin films, where intermolecular disposition is hard to predict. Chemical nature of the bridge can be used to tune electronic coupling between chromophores. In this sense, Ito and co-workers have elaborated upon simple design principle rules to tune the chromophoric couplings in covalent dimers using a Green's function approach and the partition of electronic couplings into direct and bridge-mediated contributions.<sup>446</sup>

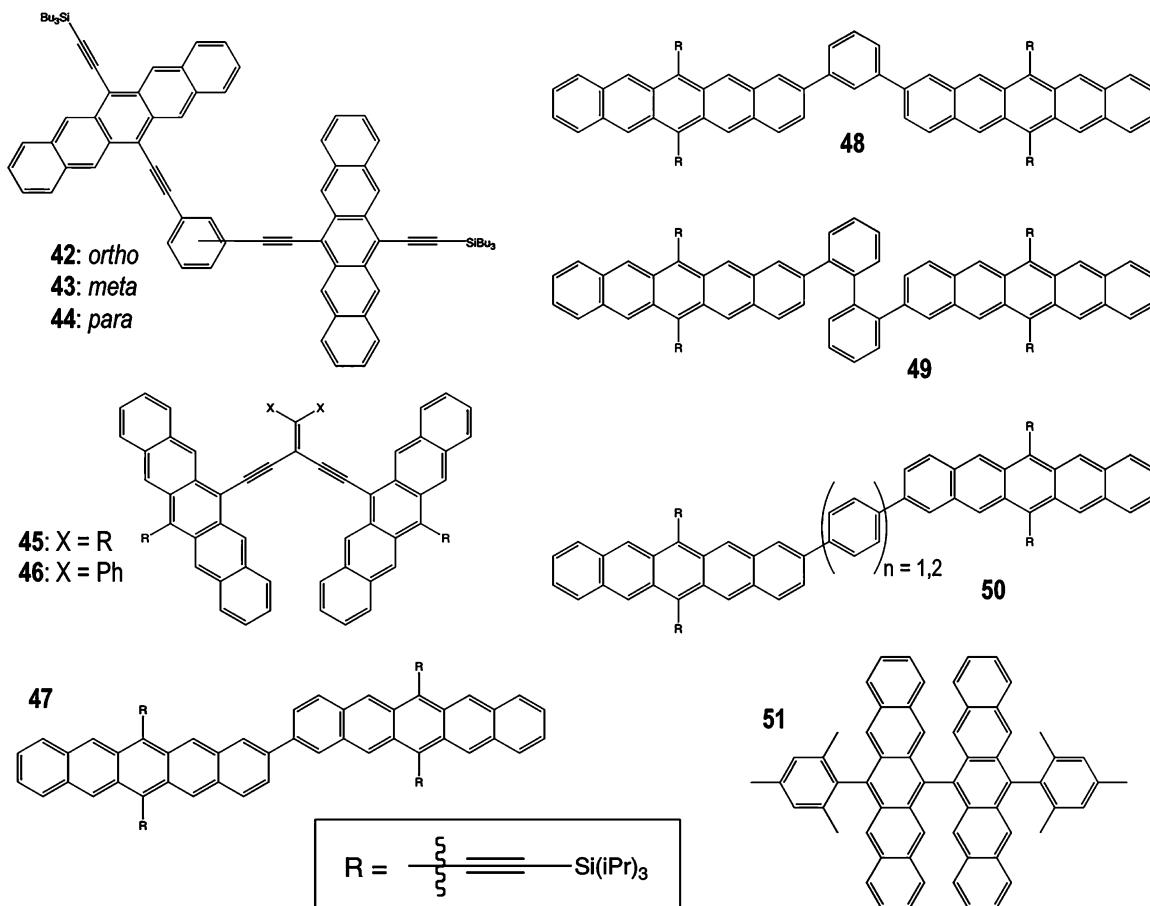
In covalent dimers, the bridging moiety can modify the singlet fission properties significantly. The linker can have a direct participation in the interaction between monomers, and in many cases, covalent linkers lead to larger electronic couplings than in the crystal. Concretely, the presence of a chemical fragment connecting the two chromophores allows for through-bond interactions not possible in molecular crystals. Computational evaluation of the through-bond couplings indicates that these can be more intense than through-space couplings.<sup>182</sup> One might expect that such an increase of electronic couplings to be beneficial for singlet fission, but, on the other hand, too strong chromophoric interaction might sensibly modify the energetics of the system toward singlet fission endothermicity.<sup>200,292</sup> Hence, it is complicated to predict fission rates in covalent dimers from separate estimation of monomeric energies and electronic couplings, and both factors must be taken simultaneously into consideration.

Delocalization of  $S_1$  state in covalent dimers is confined to two chromophores (this might not be the case in aggregates of dimers or in the solid state), which might be a source for different fission capability with respect to the crystal structure. In principle, one might argue that similar localization degree between initial and final states might facilitate internal conversion to  $^1\text{TT}$ , although this point is not clear and it has been argued that delocalization of  $S_1$  in molecular dimers can be detrimental for singlet fission due to excessive endothermicity.<sup>157</sup>

Complete singlet fission reaction requires the formation of independent triplets (second step in eq 2), which might be particularly difficult to achieve in isolated molecular dimers, since the generated triplets cannot diffuse away from each other preventing triplet–triplet fusion like in the bulk solid.<sup>447</sup> Moreover, entropy contributions favoring the triplet–triplet dissociation in solids<sup>264</sup> are not present in covalent dimers and other competing deactivation channels, such as charge-separation<sup>88</sup> or excimer formation,<sup>85</sup> might limit the fission efficiency. Besides, in these systems it might not be trivial to distinguish between weakly coupled triplets in a  $^1\text{TT}$  state, noninteracting spin-coherent triplets ( $^1\text{TT}$  with no electronic coupling), or spin-incoherent independent triplets.

The possibility of efficient singlet fission has been explored in a large variety of covalent dimers using typical singlet fission chromophores as building blocks, such as tetracene or pentacene, but also others, linked with numerous bridges (Figures 12–14).<sup>48</sup>

**Tetraene Dimers.** The first efforts dedicated to the study of molecular dimers of tetracene able to generate triplets from exciton fission were done by Bardeen and co-workers,<sup>32,33</sup> who designed and characterized several phenylene and biphenylene linked bis(tetracene) molecules (34 and 35). The study demonstrated that singlet fission is indeed possible within one (bichromophoric) molecule, although the measured intramolecular fission efficiencies were rather low (1–3%). The study concluded that the linker plays an important role in the energy relaxation on the  $S_1$  PES and has a strong impact on



**Figure 13.** Structures of singlet fission covalent pentacene dimers.

electronic couplings. Concretely, despite that the two tetracene moieties in **34** and **35** are connected with conjugated linkers, the near perpendicular disposition between the  $\pi$ -systems of the bridge and the two tetracenes results in very weak electronic couplings. Bardeen and collaborators also investigated a tetracene dimer with a xanthene bridge (**36**).<sup>282</sup> This linker induces a face-to-face disposition between tetracene moieties resulting in strong electronic coupling, but the systems do not undergo singlet fission since  $S_1$  relaxes to the formation of a very stable excimer acting as a trap state and eventually decays nonradiatively back to the ground state.

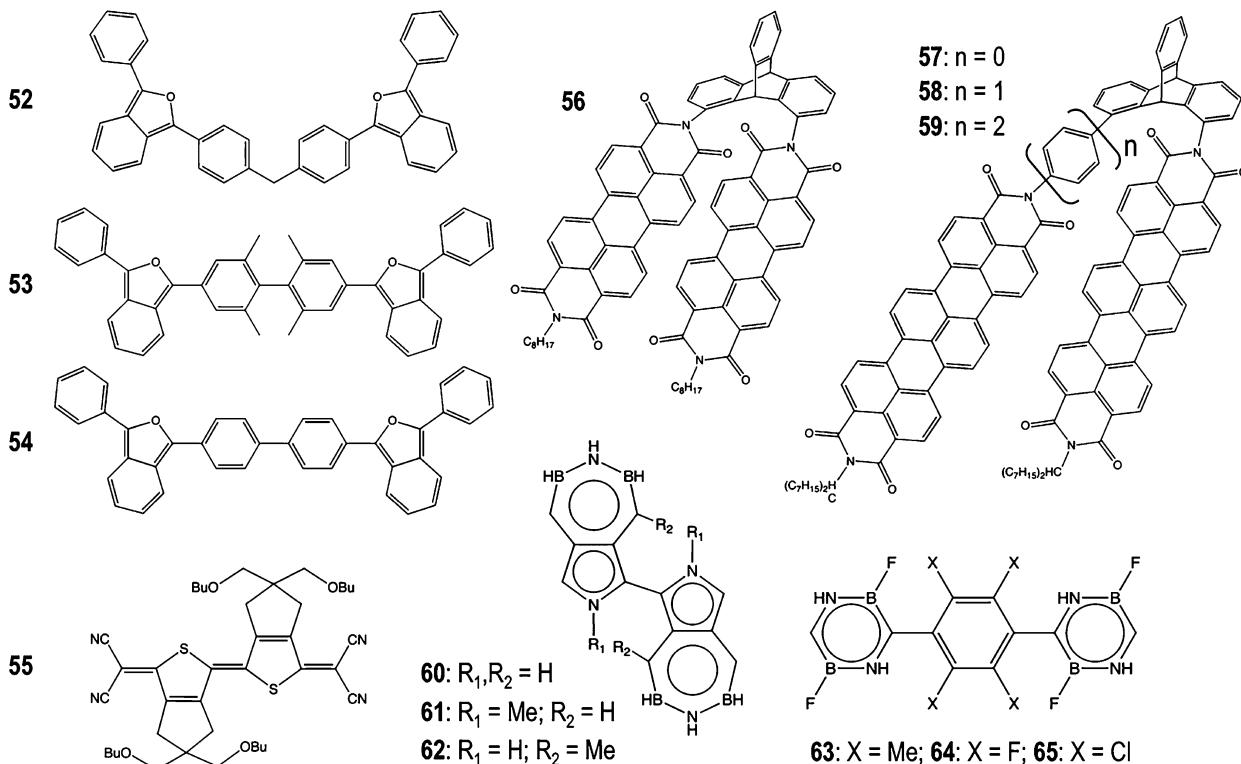
Korovina et al. synthesized and investigated the photophysics of a cofacial ethynyl-tetracene dimer chemically linked with a benzene bridging moiety (**37**).<sup>183</sup> The structural and electronic role of the linker in **37** was explored by analyzing the different excited states dynamics between **36** and **37** (xanthene vs benzene bridge). While after photoexcitation **36** decays back to the ground state very rapidly, **37** shows fast formation of  $^1\text{TT}$  in solution and high production of independent triplets (154% yield) in the solid state. As pointed out previously, the authors concluded that the strong interstate coupling in **36** is detrimental for singlet fission since it induces fast excimer or  $^1\text{TT}$  formation, but dissociation of the two triplets is strongly suppressed. The interplay between intra and interdimer singlet fission in neat films of **37** was further investigated in a separate work.<sup>181</sup> The results indicate that the formation of intra-molecular  $^1\text{TT}$  is preferred over the intermolecular multiexciton state due to larger stabilization of the former through mixing with CR configurations. These results rationalize the similar

singlet fission rates measured in solution and in the thin film. On the other hand, the interstate conversion from intra to intermolecular  $^1\text{TT}$ , probably driven by entropy factors, allows for the decoupling of triplets in the film but not in solution.

The importance of through bond-mediated electronic coupling has also been described in norbornyl-bridged tetracene dimers (**38–40**).<sup>288</sup> The results obtained for a series of molecular dimers show how delocalization of  $S_1$  favors singlet fission, highlight the hindering of  $^1\text{TT}$  formation due to symmetry reasons and point toward vibrational motions as a strategy to produce nonvanishing electronic couplings in highly symmetric conformations.

Liu et al. have investigated singlet fission in a linearly linked tetracene trimer (**41**).<sup>448</sup> The study concludes that the presence of a third tetracene unit increases the overall electronic couplings, resulting in faster and more efficient formation of triplets via singlet fission than in the bichromophoric counterpart.<sup>33</sup>

**Pentacene Dimers.** Several authors (see Figure 13) have explored theoretically and experimentally singlet fission in molecular dimers using pentacene as the chromophoric unit. The first demonstration of the formation of fission triplets in bispentacenes was achieved by Zirzlemeier et al.<sup>187</sup> The authors studied three ethynyl-pentacene dimers linked with a benzene spacer (**42–44**). Experimental evidence based on transient absorption spectroscopy and supported by ab initio calculations shows that dimers **42–44** undergo efficient intramolecular singlet fission in dilute solutions at room temperature. The study suggests some participation of CT configurations as a key



**Figure 14.** Structures of singlet fission covalent dimers 52–65.

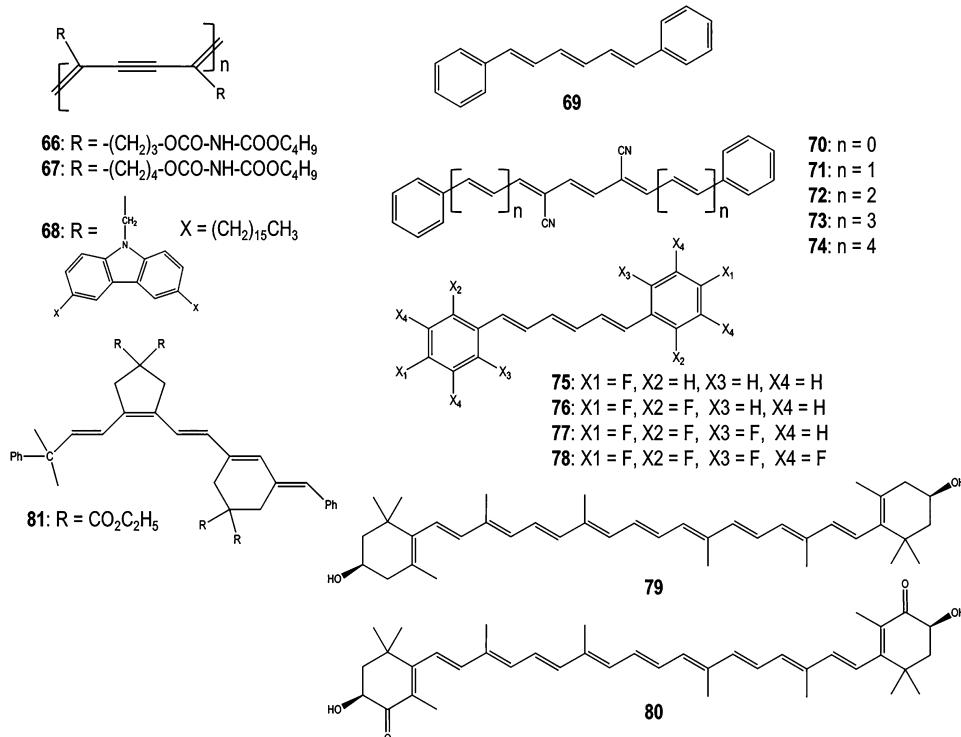
factor for the fission capabilities of these dimers and highlights the potential relevance of the through-bond coupling, in very good agreement with the conclusions obtained for the closely related bistetracene 37.<sup>181,183</sup> Later on, the same authors measured high singlet fission yields in two cross-conjugated pentacene dimers (45 and 46).<sup>449</sup> Like in molecules 42–44, through-bond interactions seem to be very important for the electronic couplings in 45 and 46, which exhibit singlet fission mediated by (virtual) CT states.

Motivated by the lack of solvent polarity dependence of singlet fission rates in pentacene dimers,<sup>450</sup> Fuemmeler et al. explored the viability of the direct intramolecular singlet fission mechanism in 47 molecules.<sup>105</sup> The linear arrangement of the two pentacene moieties results in rather weak couplings, inline with observations in linear tetracene dimers (34 and 35). But in this case, the near-degeneracy between S<sub>1</sub> and <sup>1</sup>TT boosts the formation of the multiexciton state. The authors concluded that the transition to the triplet-pair does not require mediation of CT (or CR) states, which are ~1 eV higher in energy than S<sub>1</sub> and <sup>1</sup>TT, and that in these weakly interacting dimers, singlet fission occurs through a direct mechanism. Sakuma et al. have explored the possibility of singlet fission in bent-shaped pentacene dimers (48 and 49) and found larger couplings to CT states compared to the linearly bridged dimers.<sup>451</sup> Khan and Mazumdar have employed high-order CI calculations to investigate intramolecular singlet fission in a closely related series of phenyl-linked pentacene dimers (50).<sup>452</sup> Detailed characterization of electronic states indicates that the frontier molecular orbitals of the bridge have negligible participation in the electronic transitions to S<sub>1</sub> and <sup>1</sup>TT. Moreover, differences between computed excited state absorptions of T<sub>1</sub> and <sup>1</sup>TT suggest that, in these dimers, the two triplets interact quite strongly and are unable to dissociate from the triplet-pair state.

Using a rather different molecular strategy, Lukman et al. reported fast and efficient intramolecular singlet fission in a pentacene dimer in which the two acenes are orthogonally arranged (51).<sup>453</sup> The study demonstrates that efficient formation of triplets is strongly dependent on the nuclear motion along the relaxation of S<sub>1</sub>, and that molecular rigidity, enforced by the environment, enhances the fission yields by blocking competing deactivation channels.

**Diphenylisobenzofuran Dimers.** Johnson and co-workers have intensively investigated the photophysics of covalently bonded dimers of 1,3-diphenylisobenzofuran (see Figure 14)(52–54).<sup>157,283</sup> The observed low singlet fission yields (~9%) for 52 and 53 were attributed to weak electronic couplings. In the directly coupled dimer 54, there is coexistence between localized and delocalized excited singlet that can be modulated by the solvent polarity. Localized exciton facilitates population of the triplet-pair state, while electron/hole delocalization results in energetically uphill transition to <sup>1</sup>TT and hence triplets are formed at lower efficiencies.

**Quinoidal Thiophenes.** The diradicaloid character of quinoidal oligothiophenes<sup>454–458</sup> stimulated the search for intramolecular singlet fission in these molecules. Varnavski et al. reported fast and efficient singlet fission in a tetracyanoquinodimethane bithiophene (55).<sup>180</sup> After photoexcitation, the system rapidly decays from the bright (1<sup>1</sup>B<sub>u</sub>) state to a dark (2<sup>1</sup>A<sub>g</sub>) state with coupled triplet-pair character.<sup>459,460</sup> The inversion of the energy ordering between these two states near the Franck–Condon region explains the fast population of the 2<sup>1</sup>A<sub>g</sub> state. On the other hand, the generation of two independent triplets from the 2<sup>1</sup>A<sub>g</sub> state seems unfeasible in this case, since the two triplets are strongly coupled. Although the simultaneous torsion of the two side C–C double bonds severely shrinks the triplet–triplet binding energy, such geometrical distortion seems energetically too costly to take place.<sup>184</sup> Momeni rationalized



**Figure 15.** Structures of singlet fission polyenes and carotenoids (66–81).

the different internal conversion to the dark state in quinoidal bi and tetrathiophenes by computationally exploring the energy ordering of the bright and multiexciton (dark) states along torsions of the central and side carbon–carbon double bonds.<sup>188</sup> Accurate electronic structure calculations explain the role of terminal cyano groups, why tetrathiophenes fluoresce<sup>461</sup> while 55 does not and show that dynamic electron correlations are necessary to quantify the relative energies of the low-lying excited states.

**Aromatic Diimide Dimers.** Wasielewski and co-workers have extensively explored a variety of aromatic diimides as promising candidates for singlet fission. Despite the high singlet fission yields in polycrystalline PDI,<sup>150</sup> photoactivation of cofacial PDI dimers (56) does not result in efficient generation of free triplets<sup>85</sup> due to the slight singlet fission endothermicity in PDIs, which can be overcome by entropy gain in the solid but not in isolated dimers. Moreover,  $\pi$ – $\pi$  interchromophore interactions in the dimer might result in strong stabilization of the excimer state, effectively acting as a trap state and blocking the singlet fission path.

Since the energetics of the terrylenediimide (TDI) chromophore anticipate exoergic singlet fission,<sup>87</sup> several covalent TDI dimers (57–59) have been recently investigated.<sup>88</sup> The use of a triptycene spacer in 57–59 suppresses through-bond interaction between the two linked TDIs. Interestingly, the polarity of the environment modulates the energy position of CT states with respect to S<sub>1</sub> and <sup>1</sup>TT, and in polar solvents the photoexcited dimer 59 relaxes to an intermediate state with strong (nonsymmetric) CT character, banning the access to the <sup>1</sup>TT state. On the other hand, in nonpolar solvents there is a fast population of the intramolecular coupled triplet-pair mediated by CT (or CR) configurations.

**Azaborine-Substituted Dimers.** By means of theoretical and computational design, Zeng has proposed molecular

dimers resulting from the covalent linkage of two small azaborine-substituted chromophores (60–62) previously proposed as potentially good singlet fission sensitizers.<sup>439</sup> The authors explored the optimal way to covalently connect two BN-substituted azulene molecules in order to produce fission triplets.<sup>190</sup> Electronic structure calculations and simulation of the excited state dynamics indicate that 62 might be a good candidate for fast and efficient intramolecular singlet fission, while triplet–triplet binding interaction in 60 and 61 is predicted to be too strong to produce free triplets. The same computational methodology was applied to the study of the linkage of two diazadiborine moieties through *para*-phenylene separators.<sup>345</sup> The three proposed dimers (63–65) exhibit potential singlet fission capabilities through a CT-mediated mechanism. The study reveals that the conjugated linkers directly participate in the electronic structure of the S<sub>1</sub>, CT, and <sup>1</sup>TT states. It is worth noticing that despite the promising results obtained for these dimers, the presence of atoms with high atomic numbers (i.e., chlorine in 65) could be detrimental for the singlet fission efficiencies, since they can increase the rate of the ISC deactivation path by means of the heavy atom effect on the spin–orbit couplings.

## 8.2. Polyenes and Carotenoids

The existence of the singlet fission process in carotenoids was discovered more than a decade later than in molecular crystals,<sup>20</sup> and since then, polyenes and polyene-based molecular structures such as carotenoids have been considered as alternative singlet fission chromophores.

Fundamental aspects of singlet fission in polyenes or carotenoids (e.g., states involved and fission mechanisms) are generally less well-understood than in polyacenes. Structural flexibility represents a potential limitation of singlet fission feasibility in polyenes or oligoenes, since it might open nonradiative deactivation paths to the ground state (eq 6).

On the other hand, molecular torsion of photoexcited polyenes has been suggested as a potential mechanism able to lower the rather strong triplet–triplet binding energy.<sup>462</sup> Despite recent advances in the development of theoretical models,<sup>186,463</sup> much work is necessary in order to achieve a deep understanding of the intricacies and specificities of singlet fission in polyenes and carotenoids. In particular, there is still some debate on the nature of low-lying dark electronic states in carotenoids,<sup>464</sup> which does not allow one to establish a well-defined singlet fission mechanism for these systems.

The early works of Kraabel et al. were devoted to the study of the generation of triplets via intramolecular singlet exciton fission in polydiacetylenes (**66** and **67**) (see Figure 15).<sup>465</sup> The authors considered two spin-allowed paths for the population of triplet states, that is from singlet states obtained from the absorption of one or two photons. Lanzani and co-workers investigated the singlet fission process in a closely related polydiacetylene (**68**).<sup>466</sup> Fission mechanism in **68** initiates with the population of an ionic state that decays into the (covalent) fission precursor able to split into two triplet states.

Diphenylhexatriene derivatives are paramount examples of singlet fission in carotenoids. Dillon et al. studied the fission capabilities of 1,6-diphenyl-1,3,5-hexatriene (DPH, **69**) in its monoclinic and orthorhombic crystalline forms.<sup>467</sup> Despite the fact that singlet and triplet energy levels of DPH in solution prognosticate exothermic fission, the larger redshift ( $\sim 0.25$  eV) of the lowest optically active singlet state with respect to  $T_1$  in both crystal forms results in a slightly endothermic fission reaction. The study indicates the presence of fast singlet fission in both monoclinic and orthorhombic crystals, although the excited state dynamics depend on the molecular packing. Later on, Trinh et al. reported experimental evidence of singlet fission in diphenyl-dicyano oligoenes (**70**–**74**).<sup>462</sup> On the basis of transient absorption measurements, the authors concluded that singlet fission mechanism in thin films of these carotenoids is triggered by the formation of an intramolecular triplet-pair state followed by intermolecular exciton splitting of the two triplets. The cyano substitution of DPH extends the electronic conjugation and contributes to molecular planarity enhancing intermolecular  $\pi$ – $\pi$  interactions in aggregates. Besides, electron-withdrawing character of CN groups might introduce CT character to the low-lying states, modifying the optoelectronic properties and interstate couplings. More recently, Katoh and co-workers studied the singlet fission decay path in fluorinated DPHs (**75**–**78**) by means of fluorescence quantum yields, intensity decay measurements, and magnetic field effects.<sup>468</sup> Fluorination slightly modifies the energy to the lowest optically active singlet state of DPH.<sup>469,470</sup> Like in pristine DPH, comparison of absorption profiles in solution and in the crystalline structures of **75**–**78** also exhibit a shift of the  $S_1$  energy level toward longer wavelengths, which the authors attributed to weak intermolecular interactions in the solid. Interestingly, fluorinated DPHs with slipped parallel structures (**76**–**78**) show temperature-dependent fluorescent decay rates, while **69** and **75** (herringbone packing) show no temperature dependence, once again indicating the importance of structural morphology and crystal packing in singlet fission. The authors hypothesized that the activation of symmetry breaking phononic modes in **76**–**78** crystals might be responsible for the temperature dependence in slipped parallel crystalline structures.

Tauber and collaborators observed fast triplet exciton generation through intermolecular singlet fission in carotenoid

aggregates.<sup>334,471</sup> In 2010, Wang and Tauber observed and quantified fast intermolecular singlet fission in zeaxanthin aggregates (**79**) using time-resolved resonance Raman spectroscopy.<sup>471</sup> In their study, the authors argue that singlet fission in these aggregates does not involve the population of the lowest-lying dark state ( $2^1A_g$ ). Later on, the same authors explored the singlet fission of zeaxanthin assemblies in a biological environment, that is in a lipid bilayer membrane structure, confirming the in techromophoric nature of singlet fission in these aggregates.<sup>334</sup> Musser et al. observed fast singlet fission in aggregates of astaxanthin (**80**).<sup>472</sup> In agreement with the results by Tauber and co-workers, transient absorption measurements of different aggregates indicate intermolecular singlet fission, while the monomeric species relaxes via internal conversion from the lowest-lying dark state to the molecular ground state. The authors concluded that the formation of the triplet-pair state does not require an intermediate state (e.g.,  $2^1A_g$  state), and the two fission triplets appear directly form the bright  $B_u$  band.

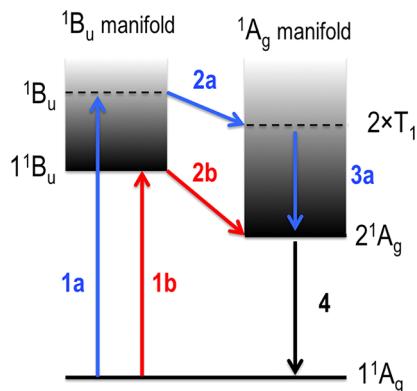
Antognazza and co-workers detected the formation of fission triplets in very long poly diethyldipropargylmalonate (**81**) through femtosecond pump–probe spectroscopy.<sup>473</sup> The formation of the long-lived triplet states requires additional vibrational energy in order to split the covalent state into two triplet excitons, otherwise the photoactivated molecule relaxes back to the ground state through internal conversion. The study predicts that triplet excitons in long polyenes extend over ten double bonds, suggesting that intramolecular singlet fission in these molecules require at least about 20 double bonds.

### 8.3. Conjugated Polymers

The spatial extension of polymers allows for the coexistence of two (or more) excitons within a single molecular chain, which opens the possibility for intramolecular singlet fission as a channel for the deactivation of singlet excitons. One of the potential advantages of polymers over standard crystalline chromophores is the possibility to structurally control the interactions between chromophoric fragments, much like in covalent dimers. In general, these compounds exhibit stronger intrachain electronic couplings than the interchain interactions formed in their aggregates or solids.<sup>474</sup> Moreover, conjugated polymers usually exhibit broad absorption bands, making them excellent light-harvesting materials.<sup>475</sup>

The generation of triplet excitons via singlet fission was observed for the first time in polymers in 1989.<sup>31</sup> The historical perspective and possible use of polymers as intramolecular singlet fission materials was nicely covered by Smith and Michl.<sup>2,3</sup> In the following, I present the main theoretical and experimental advances regarding singlet fission in polymeric compounds since then.

Musser and co-workers observed optically activated intra-chain singlet fission in poly(thienylenevinylene) (**82**).<sup>115</sup> Photoexcitation of **82** to the  $1^1B_u$  energy band edge evolves through internal conversion to  $2^1A_g$ , which decays non-radiatively back to the ground state (Figure 16). On the other hand, promotion to higher energies within the  $1^1B_u$  manifold results in the formation of a higher  $1^1A_g$  state corresponding to two coupled triplet excitons on a single polymer chain. This state might rapidly relax to the lower  $2^1A_g$  unless the triplets diffuse through interchain triplet exciton transfer. Zhai et al. also identified intrachain singlet (hot) excitation fission in polydiacetylene (**83**).<sup>476</sup> On the other hand, the same authors concluded that singlet fission in poly-



**Figure 16.** Schematic representation of the singlet fission mechanism proposed for **82** adapted from ref 115. Copyright 2013 American Chemical Society. Numeric labels correspond to excitation to midband (1a) and to band edge (1b), fission to two triplets (2a) and internal conversion (2b), recombination of triplets (3a), and nonradiative decay (4).

(dioctyloxy)phenylenevinylene (**84**) is of interchain character, since it takes place in films but not in solution.

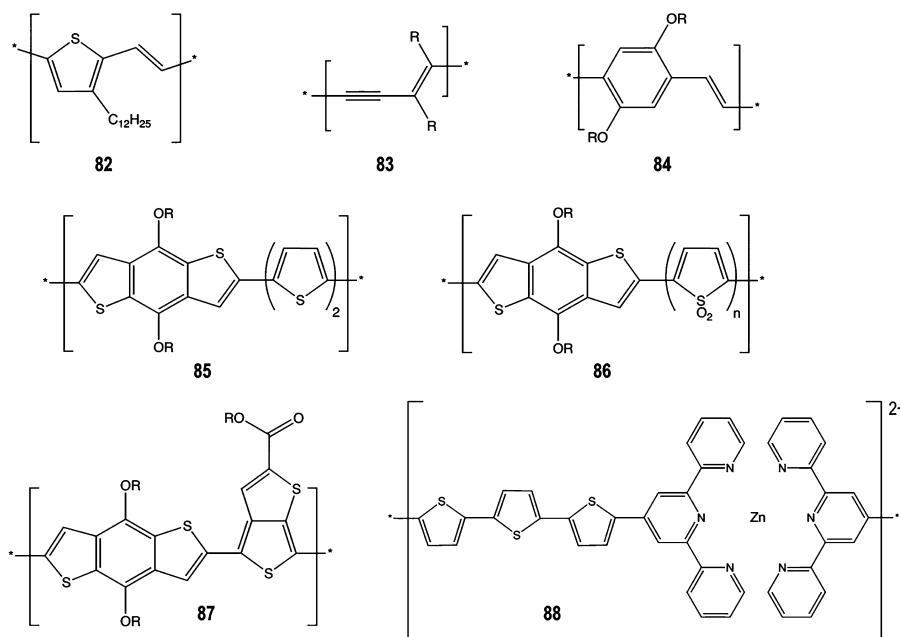
Encouraged by the idea that the presence of CT configurations mediates singlet fission and recognizing that optical excitations of push–pull polymers formed by the combination of electron-rich and electron-deficient moieties hold notable CT character,<sup>477</sup> Busby et al. designed two donor–acceptor copolymers using benzodithiophene and bithiophene or thiophene-1,1-dioxide (TDO) as donor and acceptor units, respectively (**85** and **86**) (see Figure 17).<sup>478</sup> Since TDO is able to host low-energy triplets, the two excitons generated through fission are localized on the electron-deficient units. The oxidation state of sulfur atom in TDO plays a crucial role, allowing for the fast internal conversion to multiexciton and to dark states, not available with (unoxidized) thiophene as the acceptor moiety.<sup>82</sup> Like in other polymeric systems and in oligoenes,<sup>462</sup> molecular confinement in isolated chains induces

fast recombination of the generated triplets. The study demonstrates that donor–acceptor copolymers with the right singlet–triplet energetics and with a bright state possessing strong CT character are able to achieve efficient intramolecular singlet fission. Kasai et al. observed the formation of singlet fission triplets from a hot singlet exciton in a closely related low-bandgap polymer (**87**).<sup>479</sup>

The theoretical foundations of singlet fission in donor–acceptor copolymers were further developed by Aryanpour et al.,<sup>194</sup> which computationally explored the nature of triplet-pair state in these systems. Their study reveals strong mixings of the <sup>1</sup>TT state with single-electron states due to symmetry breaking, resulting in dipole-allowed transition to the coupled triplet-pair, which would explain the two close-lying absorptions observed in low-band gap polymers.<sup>480,481</sup>

At this point, it is not clear if the lowest <sup>2</sup>1A<sub>g</sub> state in copolymers constitutes a path to singlet fission or, for the contrary, it induces nonradiative decay to the ground state as for polymer **82**. The role of this state in **86** has been recently discussed by means of density matrix renormalization group (DMRG)<sup>482</sup> calculations.<sup>197</sup> The computational results suggest that, after internal conversion to the <sup>2</sup>1A<sub>g</sub> state, both deactivation channels might compete. As the donor–acceptor strength of the copolymer increases, the triplet-pair character of the lowest dark state also increases and the binding energy between the two triplets decreases, hence favoring the singlet fission path.

Rais and collaborators identified fast singlet fission in a metallo-supramolecular polymer (**88**) by the coordination of Zn<sup>2+</sup> ions to bis(terpyridine-4'-yl)terthiophene ligand.<sup>483</sup> In this case, since S<sub>1</sub> is energetically lower than the coupled triplet-pair state, the system requires photoexcitation to the next optical state (S<sub>2</sub>) in order to be able to access the <sup>1</sup>TT state and fission into two triplets. The zinc-supramolecular polymer **88** exhibits relatively short lifetimes for the fission triplets due to triplet–triplet recombination, as commonly observed in polymers. Excitation of thin films of the pristine bis(terpyridine-4'-yl)terthiophene evolves into an excimer-like state with large



**Figure 17.** Structures of singlet fission conjugated polymers (**82**–**88**).

stabilization energy that effectively acts as a trap state blocking the singlet fission mechanism. Therefore, the presence of the Zn<sup>2+</sup> ions appears to be of vital importance for singlet fission in 88.

#### 8.4. Molecular Solids

Solid-state materials, like molecular crystals or thin films, have been largely predominant in singlet fission. Crystalline acenes, in particular tetracene, pentacene, and their derivatives, have been the most important materials in the study of singlet fission, although molecular solids of other chromophores have emerged as efficient fission materials as well. The study of the electronic states in extended systems in relation with their optoelectronic properties has been reviewed by many authors,<sup>15,123,124,356,484–490</sup> and pivots around the exciton concept (commonly used within the singlet fission community), defined as the collective excitation of interacting electron/hole pairs in solid state. Generally speaking, excitons in solids are classified in Frenkel and CT excitons, although in reality, low-lying excitations in molecular crystals correspond to the combination of these two types of states,<sup>123</sup> as many studies on singlet fission have shown.

Experimental investigations have demonstrated how variations on the crystal morphology, induced by different chemical substitution or due to different polymorphs, controls relative energetic levels and electronic couplings and hence can be used to optimize the singlet fission capabilities of organic chromophores.<sup>91,242,491,492</sup> In particular, many of these studies agree with the idea that the slip-stacked intermolecular conformation is good for singlet fission.<sup>150,242</sup>

Computational investigations on the influence of crystal packing in singlet fission have put a lot of attention on the evaluation of electronic couplings and fission rates using simple dimer or molecular cluster models,<sup>86,240,278,493</sup> which can be a good first approximation to understand the details of the formation mechanism of the triplet-pair state. On the other hand, the nature of the embedding background can have quantitative or even qualitative implications for singlet fission. Petelenz and Snamina have developed a multiscale approach in order to explicitly include the affects of the crystal environment in dimer models.<sup>494,495</sup> Application of this methodology to crystal pentacene shows the importance of the crystal field in order to stabilize CT configurations, which strongly influences electronic couplings and the energy of S<sub>1</sub>.

The symmetry properties of the surroundings of molecular dimers can have a major impact on its fission aptitude. The symmetry breaking of CR states can predominantly stabilize one of the two CT contributions, alleviating the destructive interference between the singlet fission channels mediated by opposite CT states.<sup>202,496</sup> Departure from the ideal crystal symmetry in polycrystalline films, at interfaces, due to crystal defects or through chemical doping<sup>497</sup> can create local sites with favorable singlet fission conditions,<sup>335,498</sup> although local symmetry losses can be also detrimental.<sup>274</sup>

So far, the use of periodic boundary conditions in electronic structure calculations of singlet fission for extended systems are much scarcer. Standard electronic structure theories in condensed matter physics cannot deal with multielectron processes, limiting their application to singlet fission. On the other hand, they are able to capture nonlocal features linked to the extended nature of the system. In this sense, Sharifzadeh et al. have employed the GW approximation and the BSE to compute energies and properties of low-lying excitons in TIPS-

pentacene.<sup>499</sup> Analysis of the theoretical results combined with spatially resolved optical absorption measurements predict delocalization of the lowest exciton over several molecules, consistent with estimated exciton delocalization in other molecular crystals, and highlight the importance of the crystal morphology. Teichen and Eaves have developed a one-dimensional exciton model within the Bethe ansatz,<sup>500</sup> which allows to access double electron–hole pair states, for the study of electronic states in molecular crystals with special interest in singlet fission.<sup>501</sup> The model has been coupled with a decomposition algorithm to measure spin-entanglement between the two triplet excitons in the multiexcitonic states. Laszlo and Kowalczyk have performed DFT tight-binding (DFTB)<sup>502,503</sup> simulations and other DFT-based calculations to explore the singlet fission occurrence in acene-linked two-dimensional covalent organic frameworks (COFs).<sup>232</sup> Their computational results suggest that COFs containing pentacene as the linker unit might present the proper conditions for singlet fission. The potential advantages of COFs rely on their stability, chemical versatility, and enhanced control over chromophore coupling with respect to molecular crystals; hence, the possibility of singlet fission in these materials is very appealing.

#### 9. SUMMARY AND OUTLOOK

In the last years, the intense research on singlet fission has produced great advances in the field. In particular, as exposed in the present review, theoretical and computational studies have largely contributed to improve our understanding of the singlet fission process by identifying relevant properties of electronic states, describing different fission mechanisms, or exploring the details of the singlet fission dynamics, and have helped to rationalize many different experimental findings. Despite these advances, there is still plenty of work that needs to be done in order to achieve the long-term goals for singlet fission. To that end, theoretical and computational efforts will continue to be of great value.

The still rather limited catalog of compounds able to undergo singlet fission has been repeatedly mentioned as one of the main deficiencies for the advance of singlet fission capabilities. Therefore, the computational screening for novel singlet fission sensitizers with improved properties should be one of the main priorities of theoreticians in the field, as is currently the case. Moreover, the use of computational tools and theoretical analysis can be used to identify novel chemical structures able to experience singlet fission, such in carbon nanotubes<sup>504</sup> or in COFs,<sup>232</sup> which might open new and promising routes for singlet fission.

Although electronic states in singlet fission have been characterized to great detail, the expected appearance of new singlet fission compounds will require the application of theoretical models for their study and to perform new calculations to understand the particularities of electronic states and mechanisms for each singlet fission system. Besides, more general aspects should be further investigated at the theoretical level, such is the role of the excimer state or the factors controlling the relationship between coherent and incoherent population of the <sup>1</sup>TT state.

In spite of some experimental and theoretical efforts trying to shed some light on the overall role of entropy in the singlet fission reaction, especially for systems not fulfilling the thermodynamic condition such as tetracene, it still remains an open question and future work is needed to definitively

quantify entropic effects. In this sense, investigations of singlet fission in covalent dimers (or oligomers) might be very helpful since they provide a unique opportunity to explore the role of the chromophoric environment on singlet fission sites. Time-resolved experiments looking at the singlet fission capabilities of dimers in solution and in extended structures obtained at different temperatures should produce different results if indeed entropic gain participates in the triplet–triplet dissociation. Separation of the two triplets could also be controlled by tuning the relative energy between triplets at the singlet fission dimers and on the host matrix. Hence, I foresee that the experimental and theoretical characterization of singlet fission time scales of molecular dimers embedded in different host chromophore matrices might help to reveal the importance of entropy in singlet fission.

Although a large variety of models have been employed so far to compute singlet fission couplings, I am convinced that there is still room for the use of other approaches dedicated to the general study of excitation energy transfer processes<sup>295</sup> to be applied to the study of singlet fission mechanism. The diabatic picture is very useful for the physical characterization of the fission mechanism, but depending on how diabatic (or quasi-diabatic) states are defined and constructed, which is not unique, the computed electronic couplings may vary sensibly. Hence, one should be cautious when interpreting the results, especially in the quantitative assessment of fission rates. On the other hand, the difficulties to compute derivative couplings between eigenstates of model electronic Hamiltonians is one of the main drawbacks of the adiabatic basis, specially in the study of excited state dynamics. I believe that establishing proper connections between adiabatic states and contributions with well-defined physical properties (diabats) can be very powerful in the study of singlet fission at the microscopic level. It is important to highlight that computational studies on the singlet fission dynamics are helping to reinterpret and revisit some of the aspects regarding the fission mechanisms and emphasize the important dynamic nature of it. So far, most of the computational studies on the singlet fission dynamics largely point to the CT-mediated mechanism as the main cause responsible for the fast population of the triplet-pair (<sup>1</sup>TT) state experimentally measured in singlet fission materials and have attributed a lesser role to the direct S<sub>1</sub> to <sup>1</sup>TT path. On the other hand, the conclusions extracted from these methodologies are strongly linked to the electronic model employed, in particular the state energies and couplings. Many of such investigations rely on the construction of (simple) effective electronic Hamiltonians within the diabatic framework, which, as discussed above, might hold some fundamental limitations for the study of singlet fission. Hence, integration of accurate electronic structure methods with reliable excited state dynamics approaches is desirable in order to proportionate even more robust results to undercover the intricacies of the singlet fission mechanism.

It is understood that the specificities of the electronic material are crucial in determining the relaxation mechanism of electronic spins, but the physical picture of spin decoherence (or relaxation) is still far from complete.<sup>505</sup> The spin disentangling between the two fission triplets (i.e., quantum decoherence) remains largely unexplored. Experimentally, spin coherence of fission triplets has been investigated by means of the oscillations observed in the delayed fluorescence of crystal tetracene<sup>72</sup> and through magneto photoluminescence experiments.<sup>506</sup> On the other hand, there is a lack of theoretical works

tackling this phenomenon. The theoretical characterization of spin decoherence between the two fission triplets requires the time-evolution modeling of entangled triplet pairs in a bath of electronic and atomic spins (i.e., the triplet excitons interacting with the environment) (electronic material), which opens coherence deactivation paths not possible in a closed quantum system.<sup>163</sup> Hence, it is necessary to consider open quantum system approaches able to model the spin interaction of triplet excitons with the electronic material (i.e., the electronic bath or environment). Adaptation of the methods typically used for decoherence of electronic spins in the frame of spintronics<sup>507,508</sup> or quantum computing<sup>509–511</sup> to the case of singlet fission would help to understand the origins of the rather long coherence times and the parameters controlling it.

Ab initio studies of excited states in solids can be very useful in the theoretical study of singlet fission and can complement the often employed dimer and oligomer approaches. These investigations can potentially provide new and further insights for the comprehension of singlet fission in molecular crystals related to the nature of the excited states in the condensed phases, which cannot be recovered by local dimeric molecular models. Computational studies of singlet fission based on periodic conditions have recently appeared in the singlet fission literature but still are rather scarce. These methods can potentially provide more details related to important phenomena for singlet fission, such as the loss of quantum coherence between fission triplets or the dissipation of excitons mediated by vibronic couplings, which are still not well-understood and require more attention.

Polymers are probably one of the less investigated singlet fission materials, specially from a computational point of view. In fact, singlet fission in polymers is less mature than in crystals or molecular dimers, and several fundamental aspects related to the electronic states involved or the fission mechanisms are not well-understood. Hence, I believe that the progress of singlet fission in polymeric systems could benefit from theoretical efforts.

The integration of singlet fission in solar cells has been obtained using intermolecular singlet fission materials. The evolution of intramolecular singlet fission in covalent dimers and polymers might help to incorporate these compounds in modular solar cells in the near future. In this sense, theoretical and computational studies will soon be necessary in order to understand and characterize the structural and electronic properties of these systems, in particular those at the interface between singlet fission compounds and the semiconductor. Although not directly involved in the singlet fission process, the good understanding of how the fission triplets diffuse through the system and controlling the key parameters for charge dissociation of triplet excitons at the interface are of great importance for the successful implementation of singlet fission in solar cell devices and need to be further investigated.

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The author declares no competing financial interest.

**Biography**

David Casanova graduated in Chemistry in 2000 (University of Girona) and in Physics in 2004 (University of Barcelona). He obtained a Ph.D. in chemistry in 2006 (University of Barcelona) under the supervision of Prof. Santiago Alvarez and Prof. Pere Alemany. He was a Fulbright postdoctoral researcher at the UC Berkeley in the group of Martin Head-Gordon (2007–2008). In 2009, he obtained a Ramón y Cajal Fellowship at the University Complutense of Madrid and at the University of Barcelona. In 2013, he was awarded with the Ikerbasque Research Fellowship at the University of the Basque Country, and since 2018, he is an Ikerbasque Research Associate at the Donostia International Physics Center. His main research interests focus on the development and implementation of electronic structure methods for the computational characterization of electronic excited states and their application to the study of photophysical and photochemical processes.

**ACKNOWLEDGMENTS**

I am grateful to Professor Anna I. Krylov for valuable insights and fruitful discussions. This project has been supported by the Eusko Jaurlaritza (project IT588-13) and the Spanish MINECO/FEDER (project CTQ2016-80955). The author also acknowledges financial support from IKERBASQUE, Basque Foundation for Science.

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