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Theoretical Modelling of the Singlet Fission Process

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Theoretical modelling of the singlet fission process

*From the gas phase to the effect of the
environment*

Luis Enrique Aguilar Suarez

university of
 groningen

faculty of science
 and engineering

zernike institute for
 advanced materials

The work described in this thesis was performed in the research group Theoretical Chemistry of the Zernike Institute for Advanced Materials at the University of Groningen, the Netherlands.

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Theoretical modelling of the singlet fission process

From the gas phase to the effect of the environment

PhD thesis

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Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

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To my family

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INTRODUCTION

Based on M. B. Smith, J. Michl. *Singlet Fission*. Chem. Rev. **2010**, 110, 6891–6936. and D. Casanova. *Theoretical Modeling of Singlet Fission*. Chem. Rev. **2018**, 118, 7164–7207.

ABSTRACT

Conversion of sunlight into electricity remains as a promising renewable technology, however improvements in their efficiencies are desired. Several alternatives have been explored and applied in photovoltaic devices in order to boost their conversion efficiencies. Among these alternatives, the deposition of a layer of materials on top of a solar cell that exhibits singlet fission has been proposed. The role of this layer is to (1) absorb the high-energy photons that otherwise would be lost due to thermalisation, and (2) to potentially generate two pairs of charge carriers per single absorb photon which, if properly harvested, could show efficiencies up to 200%. Even though efforts have been made to develop singlet fission-based solar cells, two main drawbacks still limit its full potential: the limited number of molecules known to exhibit the process and the poor knowledge on how singlet fission occurs.

In this initial chapter, we discuss briefly how the photovoltaic technology can be employed to face current environmental challenges. Then, we introduce the reader to the general concepts of singlet fission: the scheme of the process and the proposed underlying mechanisms of this conversion, as well as which classes of molecules are expected to undergo singlet fission. We also elaborate on the main drawbacks that limit its application, and that will be tackled through the chapters of this thesis. Additionally, we discuss in detail the calculation of electronic couplings, an integral part of this work, which are related to the probability of singlet fission to occur in a system. Besides providing the basic concepts for understanding the core of the following chapters, this initial chapter aims to encourage the reader to enter the intriguing world of singlet fission.

1.1. ENVIRONMENTAL CHALLENGES: HOW TO FACE THEM?

Predictions point out that if the temperature of the Earth raises above four degrees within the next years, around 43 to 58% of the current species inhabiting the planet will disappear.[1] This concern has led to nations to take action and, as a result, the Paris Agreement was adopted in 2015.[2] In this document, governments from almost 200 countries agreed to collaborate in order to keep the temperature rise well below two degrees. Among the strategies included in the document, the use of renewable technologies is a central point. Nevertheless, in April 2020, a study concluded that countries worldwide need to accelerate the implementation of policies regarding clean and renewable ways to generate electricity in order to reach the goals of the Paris Agreement.[3]

The conversion of sunlight into electricity remains as one of the most promising ways to face the current environmental challenges.[4] In fact, it has been estimated that if we were able to harvest the amount of energy that the sun delivers during one hour to the Earth's surface, we would fulfil the world's total annual energy consumption.[5] Nevertheless, artificial light-harvesting is still problematic due to the low quantum yields

shown in solar cells.[6] Therefore, ways to improve their efficiencies are needed. Several technologies to achieve this has been explored, such as quantum dots-based solar cells,[7] perovskite solar cells[8] and organic photovoltaics.[9]

Singlet fission (SF) has been explored as an alternative to enhance the current performance of solar cells and break the so-called Shockley–Queisser theoretical limit of 34%[10, 11], since in principle two pairs of charge carriers can be generated per absorbed photon. It has been estimated that the inclusion of a SF material layer to a single-junction photovoltaic device could increase its efficiency from 34% to approximately 45% if the charge carriers are effectively harvested.[12] Furthermore, simulations have predicted that the addition of a SF material could increase the efficiency of a current silicon-based solar cell by up to 4.2% absolute.[13] Nevertheless, the low number of molecules exhibiting SF and the poor understanding of how this process takes place have limited the development of SF-based solar cells. These are the two main drawbacks that will be tackled through the chapters of this thesis.

1.2. THE SINGLET FISSION PROCESS

SF is a multiexciton generation phenomenon that occurs in organic solids, and in which a photo excited chromophore splits into two triplets in an overall spin-allowed process by forming the so-called 1TT state (Figure 1.1).[14, 15] Since SF may give rise to the generation of two pairs of charge carriers per single absorbed photon, this process has been explored as an alternative scheme to enhance the efficiency of current solar cells and overcome the so-called Shockley–Queisser limit.[10, 11] Nevertheless, the number of molecules known experimentally to exhibit this process is limited. Furthermore the mechanistic details of the process are not yet well-understood and are the subject of an active area of research.[16–21]

In order for SF to be an efficient process, the following criteria must be fulfilled:[14, 22]

1. SF occurs usually on the picosecond time-scale and it has to be faster than any other competing process, e.g. radiative decay or intersystem crossing;
2. the process should preferably be isoergic or slightly exoergic (although endoergic SF has been observed in tetracene[23–25]) which means fulfilling the energetic requirement

$$E(S_1) \geq 2E(T_1); \quad (1.1)$$

3. the T_2 state in the molecule should be higher in energy than S_1 , and at least twice the energy of T_1 to avoid triplet-triplet annihilation,

$$E(T_2) > E(S_1) > E(T_1) \quad (1.2)$$

Additionally, some properties are desired from these materials, such as high stability under continuous radiation, low cost associated to their production for practical applications and long-lived triplets to ensure that the charge carriers can be harvested. Theoreti-

Figure 1.1 | Schematic representation of singlet fission. Upon absorption of a photon, a singlet excited molecule (S_1) transfers part of its energy to a neighbour in the ground state (S_0) to form two coupled triplets (1TT) in an overall spin-allowed process. Charge transfer states ($D_0^+D_0^-$ and $D_0^-D_0^+$) are believed to play an essential role in the conversion to the 1TT state. The three proposed underlying mechanisms for SF are depicted.

cal simulations can assist the design of SF-enhanced solar cells and be used to optimize the SF process in organic solids that fulfil the above mentioned requirements.[26, 27]

The simple picture in Figure 1.1 is generally accepted, but the conversion from S_0S_1 (or S_1S_0) to the 1TT state is still subject of ongoing debate. Three different mechanisms have been proposed to explain the process:[28–32] (i) the direct mechanism in which there is straight conversion via a two-electron transfer; (ii) the mediated mechanism, in which high-energy charge transfer (CT) states (D^+D^- and D^-D^+ in Figure 1.1) are believed to mix with the initial and final states enhancing their coupling through the so-called superexchange effect; and finally (iii) a two-step mechanism known as charge hopping in which CT states act as intermediates and are populated before the generation of the 1TT state. Thus, understanding how the coupled triplets are generated is crucial to design guidelines for optimising the conditions for the formation of the 1TT state.

1.3. APPLICATION IN SOLAR CELLS

During recent years, experimental works have started to demonstrate the potential of SF materials for enhancing the performance of solar cells within a variety of architectures.[33, 34] The general scheme of a SF-based solar cell is shown in Figure 1.2. The presented scheme is based on a proposed photovoltaic device by Einzinger *et al* in 2019 with a combined total exciton yield of $133\% \pm 13\%$. [35] The device consists of a solar cell (a silicon-based one) covered on the top by an interlayer. On top of this interlayer, a layer of a SF material is deposited and whose role is to absorb the high-energy photons that otherwise would be lost due to thermalisation. The process occurs as follows:[36]

1. a high-energy photon is absorbed in the SF layer. Here, a local exciton is formed in a single chromophore;
2. then, the photoexcited chromophore undergoes SF and two triplets are formed in the SF layer;
3. the formed triplets diffuse through the SF layer and are transferred to the solar cell by the interlayer;
4. once in the solar cell, the triplets become charge carriers and the electrons and holes are harvested in the respective electrical contacts, which gives an electric current.

Figure 1.2 | Depiction of a SF-based solar cell and the processes that occur within. 1) Formation of the photoexcited chromophore upon absorption of a photon in the SF material layer, 2) SF takes places generating two pairs of triplets, then 3) they diffuse through an interlayer to the solar cell forming two pairs of charge carriers. 4) The charges are finally harvested at the contacts. Adapted from M. Einzinger *et al. Nature* 2019, 571, 90–94

This device shows how SF materials can be exploited to boost the efficiency of current silicon-based solar cells. Nevertheless, improvements need to be made in order to reach

larger conversion efficiencies. This leads to the question, which SF materials can we employ?

1.4. SINGLET FISSION CHROMOPHORES AND MATERIALS

A chromophore might exhibit SF if it fulfils the energetic conditions mentioned in eqs. 1.1 and 1.2. Therefore, one can start looking for potential SF chromophores by computing vertical excitation energies of the S_1 , T_1 and T_2 states for the single molecule. Conclusions drawn from previous works have led to identifying two main classes of potential SF chromophores:[26]

Alternant hydrocarbons. Large conjugated hydrocarbons were the first known chromophores known to undergo SF. This class of closed-shell parents are suitable for SF because: (1) they exhibit a large HOMO/LUMO overlap which translates to a large exchange interaction, and (2) by increasing the conjugation length in these π -electron systems the S_1 state gets usually stabilised.[26] A depiction of the excited state order and how it changes when the conjugation is enlarged is shown in the left part of Figure 1.3. It is worth to mention that not all the acenes exhibit SF, being tetracene and pentacene the most studied compounds from the family. Actually, these two acenes are typically used as the backbone for new potential SF molecules by either substitution of carbon atoms by heteroatoms/heterocycles or by chemical functionalization. In Figure 1.4, some representative functionalized acenes are depicted.

Figure 1.3 | Excited state order of the closed-shell and biradical parents and the potential SF chromophores that can be derived from them. Adapted from I. Paci, J. C. Johnson, X. Chen, G. Rana, D. Popovia, D. E. David, A. J. Nozik, M. A. Ratner, J. Michl. *J. Am. Chem. Soc.* 2006, 128, 16546–16553.

Figure 1.4 | On the top, the two typical acenes (tetracene and pentacene) studied for SF applications. Beneath, some representative derivatives explored also as potential SF chromophores. Adapted from D. Casanova. *Chem. Rev.* 2018, 118, 7164–7207.

Biradicaloids. The second identified class of compounds known to exhibit SF are known as biradicaloids. A biradicaloid can be defined as a covalently-perturbed biradical. These types of molecules are of special interest due to the possibility of tuning the excited state order by chemical functionalization of a pure biradical parent as it can be observed in the right part of Figure 1.3. In a pure biradical parent, T_1 is the lowest state followed by S_0 , S_1 and S_2 . By altering its chemical structure, we reduce the biradical character and then S_0 gets lower in energy while for T_1 it increases.[14] This opportunity to alter the state order has made of the biradicaloids one of the most exploited classes of molecules for SF applications. A representative set of these chromophores is depicted in Figure 1.5.

Even though large alternant hydrocarbons and biradicaloids are the main identified classes, these are not the only systems where SF might occur. The search for novel systems exhibiting higher SF efficiencies became an active area of research in the last years. From the reported studies, we can identify new types of molecules, such as covalently linked dimers, polyenes, carotenoids and conjugated polymers.[26]

Identifying a chromophore that fulfils the energetic criteria in eq. 1.1 and eq. 1.2 is only the first step. We then need to analyse if SF can in a dimer which is the minimal system where the process can occur. In order to do so, we can calculate electronic couplings.

Figure 1.5 | Chemical structures of representative biradicaloids proposed for SF applications. Adapted from D. Casanova. *Chem. Rev.* 2018, 118, 7164–7207.

1.5. ELECTRONIC AND NONADIABATIC COUPLINGS

Once a potential SF chromophore has been identified to fulfil the energetic conditions in eq. 1.1 and 1.2, we can extend the analysis to the gas-phase dimer model which is the minimal required system where SF can occur. The kinetics of the SF process can be modelled as a first-order reaction.[26] Within the weak coupling limit, a rate constant (k_E) associated with the process can be approximated by means of the Fermi's golden rule,[37]

$$k_E \approx \frac{2\pi}{\hbar} |V|^2 \rho(E) \quad (1.3)$$

where V represents the electronic coupling between the initial and final (diabatic) states, and $\rho(E)$ denotes the density of states per unit of energy E . This direct relationship has led to the development of methodologies for computing V at different levels of sophistication.[26, 38] The calculation of V allows to predict SF mainly for the formation of the 1TT state from the initially photoexcited state.

The direct calculation of V between the diabatic localised states is referred to as the direct coupling (DC) scheme, which has been used in previous works to calculate electron transfer couplings.[37] The effective V can be expressed as

$$V = \frac{\langle \Phi_i | \hat{H} | \Phi_f \rangle - \frac{1}{2} (\langle \Phi_i | \hat{H} | \Phi_i \rangle + \langle \Phi_f | \hat{H} | \Phi_f \rangle) \cdot \langle \Phi_i | \Phi_f \rangle}{1 - \langle \Phi_i | \Phi_f \rangle^2} \quad (1.4)$$

where $\hat{H}$ denotes the electronic Hamiltonian, and i and f denotes the initial and final

states of interest, respectively.

In an adiabatic approximation, the nonadiabatic couplings (also known as vibronic couplings) are the key quantities to study and understand the transition between the states of interest.[39] A simple approach to estimate the nonadiabatic couplings based on the one-particle transition density matrix (1TDM, γ) between the initial (i) and final (f) states has been developed.[40] In this approach, the norm of the 1TDM (represented as $\|\gamma\|^2$) is assumed to be proportional to the nonadiabatic couplings between the states of interest, and it represented as[26]

$$\|\gamma\|^2 = \sum_{p^+q} (\gamma_{pq}^{if})^2. \quad (1.5)$$

In this expression, $\gamma_{pq}^{if} = \langle \Psi_i | p^+ q | \Psi_f \rangle$ where p^+ and q are the one-particle creation and annihilation operators, respectively.[26] This approach has been employed to understand how the SF process in perylenediimide dimers,[41] as well as on how the morphology affects SF in two different polymorphs of 1,3-diphenylisobenzofuran.[42]

Please note that both approaches, the DC scheme and calculation of $\|\gamma\|^2$, are used in this thesis.

1.6. AIM AND OUTLINE OF THIS THESIS

We have established clearly the need of exploring and applying novel alternatives to enhance the performance of current solar cells and face the environmental challenges. This thesis focuses on providing answers, aided by quantum chemistry calculations, to two of the main drawbacks of the SF process: 1) Finding novel and potential SF chromophores and 2) provide a deeper understanding of the underlying mechanism of the SF process in the crystal structures.

Finding new potential chromophores with high SF efficiencies becomes then an essential task for those of us who are dedicated to studying this process. It is clear that an experimental high-throughput screening is non-viable due to the high cost and time associated with it. Reducing the number of molecules that can be tested experimentally might be aided by means of quantum chemistry calculations. In **Chapter 2**, we identify a potential SF chromophore from a set of molecules previously reported in the literature by verifying if they fulfil the energetic condition in eqs. 1.1 and 1.2. The corresponding vertical excitation energies for the individual molecules are calculated with a variety of methods ranging from high-level theory to more computationally affordable ones. Once the potential chromophore has been spotted, we extend the analysis to a possible crystal structure. Electronic couplings for identified pair arrangements are calculated using a non-orthogonal configuration interaction approach to identify if the possible crystal structure would be a suitable candidate for SF applications. The pairs exhibit different electronic couplings which leads to also different SF probabilities to occur. This qualitative behaviour was compared against two other theoretical methods commonly used for the investigation of SF. We conclude that the qualitative trend identified for the pairs is similar for the three approaches which, in principle, validates our analysis. The calculated electronic couplings suggest that the SF process might occur in the proposed

1

crystalline structure. The finding of this chapter are an incentive not only to further study the crystal structure of the identified chromophore but also derivatives of it for future SF applications.

Electronic couplings are a key quantity related to probability of SF to occur in a system. Nevertheless, this coupling depends heavily on the spatial disposition of the molecules. This has led to the development of methods to find arrangements where the coupling is maximised. As the reader can anticipate, such methodologies rely on computationally affordable methods but whose accuracy need further validation. Comparison of electronic couplings calculated with a so-called simple method (based on a frontier orbitals approach) against a high-level theory one is the scope of **Chapter 3**. Here, a high throughput screening of dimer dispositions was performed with the simple method which resulted in 48 potential pair arrangements. Then, electronic couplings for these 48 structures were calculated employing the *ab initio* Frenkel-Davydov exciton model. In this chapter, we will discuss the correlation between the electronic couplings and the Davydov splitting calculated with the simple and *ab initio* methods. Even though a perfect linear correlation is not observed, we confirm that the dispositions with the largest couplings in the simple method also have the largest *ab initio* electronic couplings. Results of this chapter point to the use of the simple method for performing a preliminary search of dimer dispositions which can be then studied with a higher level of theory. Once it has been confirmed that in these dispositions the coupling is maximised, this could be the basis for engineering novel crystal structures with higher SF efficiencies.

Calculation of electronic couplings, which are related to the probability of SF to occur in a system, are of great importance for the study of the process. Nevertheless, exploring the character of the excited states on these systems might offer a new insight on the underlying mechanism, and at the same time can offer a predictive power for the optimisation of the dimer arrangements. An excited state analysis of the SF process is widely discussed in **Chapter 4**. First, we establish a suitable theoretical methodology for the study of excited states on a tetracene molecule. Then, we expand our study to include dimer arrangements identified in the crystal structure of tetracene. It is demonstrated that the excited state character is different for dimers with larger and lower electronic couplings. It is also demonstrated how the excited state analysis can be employed to offer a new perspective on the study of SF materials.

A gas phase dimer model is typically employed to study SF and it has proved its utility as a first-approximation to study the process. Nevertheless, in certain cases this minimal simple model is not enough to capture the physics and influence that the surrounding crystal packing has on the character of the excited states. Therefore, going beyond the gas phase model becomes necessary particularly to explain experimental observations where SF efficiency depends on the crystal packing. In **Chapter 5** we study the influence of the crystal packing on the electronic couplings, the so-called excitons descriptors and *electron-hole* correlation plots and in the overall qualitative description of the SF process. We employ the excited state analysis to unravel differences between two polymorphs of a chromophore which exhibit different SF yields. The polymorphs have similar crystal packing with differences arising solely from intermolecular interactions in the next-nearest neighbours which stresses the importance of going beyond the gas-phase dimer model. Results point to different excited state character in the two polymorphs which

might explain their different SF conversion efficiencies. The findings of this chapter suggest that the excited state analysis can be used to study the excited states of crystalline solids and might offer answers to experimental observations.

1

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FINDING NEW POTENTIAL SINGLET FISSION CHROMOPHORES

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ABSTRACT

Singlet fission materials are considered as a potential alternative to enhance the performance of solar cells. It has been proved that adding a layer of one of these materials to a photovoltaic device could improve its conversion efficiency. Nevertheless, the number of molecules known to exhibit this phenomenon is low due to the strict energetic requirements that the molecules must fulfil. Therefore, finding or designing novel materials that have potential singlet fission applications becomes one of the first and major challenges that need to be addressed. Tackling this challenge is the scope of this chapter.

*Here, we discuss the non-orthogonal configuration interaction approach and how this can be applied for the calculation of electronic couplings for pairs of molecules identified within the crystal structure of a molecule. Additionally, we compare the results of the non-orthogonal approach against two other theoretical methodologies commonly employed for the description of singlet fission: the restricted active space with two spin flips method and the *ab initio* Frenkel-Davydov exciton model. First, we focus our attention on a tetracene dimer, a widely studied molecule known to exhibit singlet fission. We conclude that the three studied approaches show a similar qualitative agreement for this dimer. After we have established this comparison, we identify a novel singlet fission molecule from a set of previously reported candidates. Such identification is based on excitation energies calculated with different levels of theory. Dimer arrangements are identified within a proposed crystal structure of the molecule. Results suggest that the identified molecule has potential for SF applications.*

2.1. INTRODUCTION

Since the first observation of singlet fission (SF) in anthracene crystals back in 1965,[1] the search of novel SF materials remains as an active area of research. The low number of molecules known to undergo this process is one of the main limitations for applying SF in photovoltaic technologies. One of the reasons behind this small number of materials is the critical energy conditions in eqs. 1.1 and 1.2 that the single molecule is expected to fulfil. Finding (or designing) molecules that nearly satisfy these energetic requirements is a major challenge that needs to be addressed.

Theoretical simulations can assist in finding novel molecules that fulfil the above mentioned energetic requirements. The first step would be to compute the excitation energies of the lowest singlet excited (S_1), the lowest triplet (T_1) and second triplet (T_2) states. In order to facilitate the selection of potential SF molecules from a large set of candidates, one can define a new energy parameter, E_{stt} , as

$$E_{stt} = E(S_1) - 2E(T_1). \quad (2.1)$$

SF should be, in principle, and isoergic process[2] which means that E_{stt} must be ideally close to zero for a given molecule. Nevertheless, studies have suggested that the process might occur even if it is slightly endo or exoergic.[3–5] These observations imply that for a molecule to be considered as a potential SF candidate its value of E_{stt} should be roughly close to zero within some acceptable range.

Theoretical efforts have been done in the last years to spot potential SF molecules.[6–11] The focus of these works is to narrow the number of molecules from a relatively large library (or set) of candidates.[12, 13] As the reader might infer, low-accuracy yet computationally affordable methods (with a previous benchmark study) are needed for such large scale screenings. For example, time-dependent functional theory[14] (TD-DFT) was employed to calculate the S_1 and T_1 excitation energies of a library consisting of 40 thousands candidates. Based on the results, nearly 200 molecules from the library were identified to fulfil the energy condition $E(S_1) \geq 2E(T_1)$ and were proposed for further studies.[9] In another study, 88 SF candidates were identified from a set of almost 4500 anthracene derivatives based also on TD-DFT calculations.[15]

Besides the large screening of molecules, studies in smaller sets of candidates with high-level accuracy methods have been performed in order to find suitable SF materials. For instance, five biradicaloid heterocycles were studied as initial candidates for SE.[16] Adiabatic excitation energies of the S_1 , S_2 , T_1 and T_2 states for each of these chromophores were calculated using an accurate quantum chemical method, namely complete active-space second-order perturbation theory (CASPT2). This work concluded that two out the five studied chromophores fulfilled the energy conditions in eqs. 1.1 and 1.2, and they were proposed as potential candidates for further experimental evaluation. A subsequent theoretical study on the crystalline structure of one of these molecules (1,4-dimethylpyrazine-1,4-dium-2,5-bis(olate)) has encouraged its potential for SF applications.[17]

Spotting a chromophore that fulfils the energetic requirement is not sufficient. Evaluating a single molecules is not enough since the minimal system where SF can occur is a dimer. Therefore, studying the process in clusters of molecules becomes necessary. As explained in Section 1.5, the conversion from the S_0S_1 to the 1TT state can be modelled as a first order reaction, and its probability to occur can be approximated as a rate constant. This constant is proportional to the electronic coupling between the initial and final states, that in the case of SF correspond to the S_0S_1 (or S_1S_0) and 1TT states, respectively. These electronic couplings can be calculated for identified dimer arrangements in the corresponding crystal structures to determine if it has potential as a SF material.

The outline of this chapter is as follows: In Section 2.2.1 we describe in more detail the approach used for the calculations of the effective electronic couplings in the identified pairs of the chromophores studied in this chapter. Additionally, in Sections 2.2.2 and 2.2.3 we explain the theory behind two other approaches used commonly in the description of the SF process. First, we focus our attention on tetracene, a widely studied chromophore known to exhibit SF in the crystal structure. We compare the qualitative performance of the three approaches. Results for the comparison on the tetracene pair are discussed in Section 2.3.1. After this comparison, in Section 2.3.2 a potential SF chromophore is chosen from a set of candidates based on whether they fulfil or not the energy conditions in eq. 2.1 and 1.2. The excitation energies of the corresponding molecular states were cal-

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culated employing TD-DFT with different functionals, as well as with the following wave function-based methods: (1) scaled-opposite-spin configuration interaction singles with a perturbative account of double excitations (SOS-CIS(D));[18] 2) complete active space self-consistent field with correction to the energy using second-order perturbation theory (CASSCF/CASPT2),[19] and 3) the second-order algebraic diagrammatic construction scheme[20] (ADC(2)) of the polarization propagator.

Once the novel chromophore is determined, dimer arrangements are identified within a proposed crystal structure. Comparison of the three methodologies on the new chromophore is discussed in Section 2.3.3. Finally, the concluding remarks and further investigations are mentioned in Section 2.4.

2.2. THEORY

2.2.1. NON-ORTHOGONAL CONFIGURATION INTERACTION APPROACH

In the non-orthogonal configuration interaction (NOCI) approach, a solid is described in terms of molecular states. Therefore we calculate, for different electronic states of each molecule in an ensemble, molecular wave functions that are subsequently combined into basis functions which describe a particular combination of molecular states. The final wave function for the ensemble is then written as an expansion of these many-electron basis functions (MEBFs). The NOCI approach is attractive for the description of SF since the wave function is constructed with MEBFs that describe all the states involved and, moreover, the interaction between the photo excited state and the multi exciton state can be directly calculated. The molecular wave functions can be chosen to be CASSCF wave functions in which both the orbitals and CI coefficients are fully optimized. Each molecular wave function is optimized with its own set of orbitals and represent a specific electronic state I of molecule A (Ψ_A^I), such as the ground state ($\Psi_A^{S_0}$), the lowest singlet excited state ($\Psi_A^{S_1}$), the lowest triplet state (Ψ_A^T), the cationic ground state ($\Psi_A^{D_0^+}$) and the anionic ground state ($\Psi_A^{D_0^-}$). The MEBFs ($|\Phi_\mu\rangle$) are then constructed as spin-adapted antisymmetrized products of the molecular wave functions:

$$|\Phi_\mu\rangle = \sum_{\sigma} \kappa_{\sigma} \hat{A} \prod_A^N |\Psi_A^I\rangle_{\sigma} \quad (2.2)$$

where N is the number of molecules in the ensemble, κ_{σ} are the corresponding spin-coupling coefficients, and the summation over σ indicates that several antisymmetrized products of molecular wave functions with different M_s eigenvalues are combined such that the resulting MEBFs are spin eigenfunctions. In practice, for example for a pair of molecules, a MEBF is generated from the molecular CASSCF wave functions as:

$$\hat{A} \left(\sum_i C_i^A \Delta_i^A \right) \left(\sum_j C_j^B \Delta_j^B \right) = \sum_{ij} C_i^A C_j^B \hat{A} |\phi_{\mu}^A \dots | | \phi_{\nu}^B \dots | = \sum_{ij} C_i^A C_j^B |\phi_{\mu}^A \dots \phi_{\nu}^B \dots|. \quad (2.3)$$

In this notation, C_i and C_j denote the CI coefficients of the molecular CASSCF wave functions, Δ is a Slater determinant, and ϕ indicates the occupied spin orbitals in the

Slater determinant for molecules A and B. In principle, the number of molecules included in the ensemble is not limited. However, our preliminary investigation following the protocol outlined in Ref. [21], for a pair of molecules taken from the structure reported in Ref. [21], resulted in an electronic coupling between the photo excited and the multi exciton state of 9 meV, compared to 12 meV reported for a cluster of three molecules; this indicates that the size of the ensemble only marginally affects the electronic coupling. Therefore, in this chapter we focus on the study of pairs of molecules.

In a pair of molecules named as A and B, several MEBFs can be constructed, e.g., one MEBF describing both molecules in their ground state ($|\Phi_{S_0S_0}\rangle$); two MEBFs in which one of the molecules is in the lowest singlet excited state ($|\Phi_{S_0S_1}\rangle$ and $|\Phi_{S_1S_0}\rangle$); one MEBF representing the two triplets coupled into a singlet ($|\Phi_{1TT}\rangle$); and two MEBFs describing the charge transfer (CT) states ($|\Phi_{D_0^+D_0^-}\rangle$ and $|\Phi_{D_0^-D_0^+}\rangle$). The three spin singlet MEBFs constructed from the molecular wave functions with $S = 0$ are formed as:

$$|\Phi_{S_0S_0}\rangle = \hat{A}|\Psi_A^{S_0}\Psi_B^{S_0}\rangle \quad (2.4a)$$

$$|\Phi_{S_0S_1}\rangle = \hat{A}|\Psi_A^{S_0}\Psi_B^{S_1}\rangle \quad (2.4b)$$

$$|\Phi_{S_1S_0}\rangle = \hat{A}|\Psi_A^{S_1}\Psi_B^{S_0}\rangle \quad (2.4c)$$

whereas, the MEBFs constructed from the molecular wave functions with $S > 0$ (i.e. Ψ^T , $\Psi^{D_0^+}$ and $\Psi^{D_0^-}$) are expressed as linear combinations of the antisymmetrized products of those molecular functions, in such a way that the total M_s and S are equal to 0[22]:

$$|\Phi_{1TT}\rangle = \frac{1}{\sqrt{3}}\hat{A}|\left(\Psi_A^T\right)_{M_s=+1}\left(\Psi_B^T\right)_{M_s=-1}\rangle + \frac{1}{\sqrt{3}}\hat{A}|\left(\Psi_A^T\right)_{M_s=-1}\left(\Psi_B^T\right)_{M_s=+1}\rangle - \frac{1}{\sqrt{3}}\hat{A}|\left(\Psi_A^T\right)_{M_s=0}\left(\Psi_B^T\right)_{M_s=0}\rangle \quad (2.5a)$$

$$|\Phi_{D_0^+D_0^-}\rangle = \frac{1}{\sqrt{2}}\hat{A}|\left(\Psi_A^{D_0^+}\right)_{M_s=+1/2}\left(\Psi_B^{D_0^-}\right)_{M_s=-1/2}\rangle - \frac{1}{\sqrt{2}}\hat{A}|\left(\Psi_A^{D_0^+}\right)_{M_s=-1/2}\left(\Psi_B^{D_0^-}\right)_{M_s=+1/2}\rangle \quad (2.5b)$$

$$|\Phi_{D_0^-D_0^+}\rangle = \frac{1}{\sqrt{2}}\hat{A}|\left(\Psi_A^{D_0^-}\right)_{M_s=+1/2}\left(\Psi_B^{D_0^+}\right)_{M_s=-1/2}\rangle - \frac{1}{\sqrt{2}}\hat{A}|\left(\Psi_A^{D_0^-}\right)_{M_s=-1/2}\left(\Psi_B^{D_0^+}\right)_{M_s=+1/2}\rangle. \quad (2.5c)$$

Then, the total NOCI wave function (Ψ_{NOCI}) describing the ensemble is expressed as a linear combination of the different MEBFs:

$$\Psi_{NOCI} = \sum_{\mu} C_{\mu}|\Phi_{\mu}\rangle \quad (2.6)$$

in which the coefficients C_μ are determined using variational theory and can be related to a weight for each MEBF that indicates the importance of a particular combination of molecular electronic states in the description of an electronic state of the ensemble. To perform such a calculation the Hamiltonian $\langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle$ and overlap $\langle \Phi_\mu | \Phi_\nu \rangle$ matrix elements are needed. The MEBFs are mutually non-orthogonal, since they are constructed from independent and fully optimized molecular wave functions. Note that each $|\Phi_\mu\rangle$ consists of multiple determinants and therefore for the calculation of $\langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle$ a large number of Hamiltonian matrix elements over determinant pairs has to be evaluated; this becomes the main computational challenge. The Hamiltonian and overlap matrix elements can be then used to calculate the electronic coupling, according to the direct coupling scheme[21]

$$V_{\mu\nu} = \frac{\langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle - \frac{1}{2} (\langle \Phi_\mu | \hat{H} | \Phi_\mu \rangle + \langle \Phi_\nu | \hat{H} | \Phi_\nu \rangle) \cdot \langle \Phi_\mu | \Phi_\nu \rangle}{1 - \langle \Phi_\mu | \Phi_\nu \rangle^2} \quad (2.7)$$

where Φ_μ and Φ_ν denote the initial and final (diabatic) states of interest, respectively, which in the case of SF correspond to the photo excited states and the two coupled triplets. The Hamiltonian in eq. (2.7) is the Hamiltonian for the ensemble within the Born-Oppenheimer approximation. Please note that the MEBFs are denoted as $|\Phi\rangle$ whereas the electronic states are denoted by Φ .

2.2.2. RESTRICTED ACTIVE SPACE WITH TWO SPIN FLIPS METHOD

The restricted active space with two spin flips (RAS-2SF) calculations for the dimer arrangements were performed with an active space of four electrons in four orbitals (RAS(4,4)-2SF) using a high-spin quintet as the initial reference.[23] The resulting dimer wave functions ($|\Phi\rangle$) are then described in terms of different configurations; local excited ($|\Psi_{LE}\rangle$), multi excitonic ($|\Psi_{1TT}\rangle$) and CT states or charge-resonance ($|\Psi_{CT}\rangle$);

$$|\Phi\rangle = C^{LE} |\Psi_{LE}\rangle + C^{1TT} |\Psi_{1TT}\rangle + C^{CT} |\Psi_{CT}\rangle \quad (2.8)$$

where C^{LE} , C^{1TT} and C^{CT} are the corresponding amplitudes of the LE, CT, and $1TT$ configurations. The importance of each configuration in the different states is described by the corresponding weights (ω_i), calculated as the square of their amplitudes ($\omega_{LE} = |C^{LE}|^2$, $\omega_{1TT} = |C^{1TT}|^2$ and $\omega_{CT} = |C^{CT}|^2$). Based on these weights, $\Phi_{[1]}$ and $\Phi_{[2]}$ states are assigned to those wave functions with large ω_{LE} , whereas the Φ_{1TT} corresponds to the one with large ω_{1TT} . Then, the norm of the one-particle transition density matrix ($||\gamma||^2$) is used to estimate the couplings between singlet excited and $1TT$ states.[24]

2.2.3. *ab-initio* FRENKEL-DAVYDOV EXCITON MODEL

The non-orthogonal *ab initio* Frenkel-Davydov exciton model (AIFDEM) methodology follows, in principle, the same protocol as the NOCI approach. For each pair of molecules, molecular wave functions are generated and then, MEBFs describing the electronic states of the ensemble are constructed as direct products of those molecular wave functions. In AIFDEM, Hartree-Fock wave functions are used for the description of the S_0 , D_0^+ and D_0^- states and CIS wave functions for the S_1 and T_1 states.[25] As in NOCI, six different MEBFs were generated: $|\Phi_{S_0S_0}\rangle$, $|\Phi_{S_1S_0}\rangle$, $|\Phi_{S_0S_1}\rangle$, $|\Phi_{1TT}\rangle$, $|\Phi_{D_0^+D_0^-}\rangle$ and $|\Phi_{D_0^-D_0^+}\rangle$. Then, the total wave function of the ensemble is expanded as a linear combination of the MEBFs, and the CI coefficients (C_μ in eq. (2.6)) are determined using variational theory. The resulting CIS and Hartree-Fock energies were corrected, as outlined in the protocol in Ref. [26], by shifting the diagonal elements of the Hamiltonian matrix in the orthogonalized[27] basis to match reference values calculated for an optimized molecule at the ω B97X-D/cc-pVDZ level of theory. The $\langle\Phi_{S_0S_1}|\hat{H}|\Phi_{S_0S_1}\rangle$ and $\langle\Phi_{S_1S_0}|\hat{H}|\Phi_{S_1S_0}\rangle$ elements were shifted to match the vertical S_1 excitation energy, whereas the $\langle\Phi_{1TT}|\hat{H}|\Phi_{1TT}\rangle$ element was shifted to twice the T_1 excitation energy. It has been shown in a benchmark study that among various popular functionals, the ω B97X-D functional gives the best description of excited state properties when compared to high-level wave function methods.[28–30]

The $\Phi_{D_0^+D_0^-}$ and $\Phi_{D_0^-D_0^+}$ energy reference values were approximated as the sum of three terms; ionization potential (IP), electron affinity (EA) and the Coulombic attraction (CA). IP and EA were calculated from the energies of the neutral, cationic and anionic form of a molecule at the ω B97X-D/cc-pVDZ level of theory, whereas the CA was determined as the electrostatic attraction between the centers of mass of the molecules in the corresponding cationic and anionic ground states. The weights of each MEBF were calculated similarly to the NOCI approach.

2.3. RESULTS AND DISCUSSION

2.3.1. COMPARING NOCI, RAS-2SF AND AIFDEM FOR TETRACENE

A pair of tetracene molecules, an extensively studied singlet fission molecule,[31, 32] has been used to compare the NOCI approach with RAS-2SF and AIFDEM before studying unexplored systems. Figure 2.1 shows the orientation of the tetracenes in the tetracene dimer arrangement.

The methods are compared in three aspects:

- **Excited state energies:** This would determine if there are CT states present, and if they act as real or virtual intermediaries, and hence, determine the underlying SF mechanism,
- **Weights of MEBFs.** In order to determine if the methods predict similar character for the studied electronic states, and,
- **Electronic couplings.** Different electronic couplings for the pairs translates to different SF probability to occur. The comparison aims to determine if the methods show a similar qualitative trend regarding the SF probabilities.

Figure 2.1 | Tetracene dimer arrangement; d = centers of masses distance, θ = angle between the molecular planes.

The calculated state energies and the individual contributions for the tetracene dimer arrangement are shown in Table 2.1 and Table 2.2, respectively. The energies in Table 2.1 were calculated in the gas-phase, whereas the reported experimental values correspond to determinations in solution[33, 34] for S_1 and T_1 and in the crystal structure for the CT states[35].

Excited state energies. The energies calculated with the NOCI approach are reported in Table 2.1. For the sake of computational cost, we have restricted the active space of the molecular wave functions to four electrons in four orbitals (denoted NOCI:CASSCF(4,4)). The NOCI energies are overestimated when compared to the experimental values. The energies might be improved by adding the remaining π - and π^* -like orbitals to the active space. RAS-2SF also overestimates the energies of the electronic states because of an incomplete account of dynamic correlation,[36] and as in the NOCI approach, the energies are expected to improve by increasing the active space. The energies calculated with AIFDEM have been corrected as explained in Section 2.2.3; these energy values are also overestimated.

The overestimation of the energies for the three methods might be due to the fact that the calculations are performed without the environment effects, neither the solvent nor the surrounding crystal structure. Despite this overestimation, the results suggest that the CT states are too high in energy to be accessed but perhaps act as virtual states promoting a charge transfer-mediated superexchange mechanism (see Figure 1.1).

Table 2.1 | State energies (in eV) of the different electronic states for a pair of tetracene molecules. For AIFDEM, the unshifted values are reported in parenthesis. The calculated $\Phi_{[2]}$ state with RAS-2SF is dominated by the $|\Phi_{S_1 S_1}\rangle$ configuration and is not included.

Method	Φ_{1TT}	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi_{D^+D^-}$	$\Phi_{D^-D^+}$
NOCI:CASSCF(4,4)	3.96	4.30	4.41	4.71	5.42
NOCI:CASCI ^{Ref.[21]}	4.12	4.45	4.49	4.94	5.03
RAS(4,4)-2SF	3.52	4.11		5.00	
AIFDEM	3.20(4.39)	3.20(3.78)	3.26(3.86)	3.50(3.42)	3.52(4.13)
Experimental	2.54 ^{Ref. [33]}	2.62 ^{Ref. [34]}	2.62 ^{Ref. [34]}	2.90 ^{Ref. [35]}	2.90 ^{Ref. [35]}

The calculated state energies in this chapter are compared with previously reported values[21] in which a NOCI calculation was performed for a cluster of three tetracene molecules (values denoted as NOCI:CASCI in Table 2.1). Unlike here, where we generate proper spin-adapted, antisymmetrized products of molecular wave functions as the MEBFs, in that work MEBFs were approximated by CASCI wave functions: the orbital sets resulting from molecular CASSCF(4,4) wave functions were projected on the basis of the trimer, followed by orthogonalization and a CASCI(12,12) calculation. This procedure results in MEBFs, contaminated with small contributions of (unwanted) CT states. Differences between the results in state energies and electronic couplings in this chapter and Ref. [21] can be attributed to differences in the geometry of the ensemble (Ref. [21] used a B3LYP/6-21G optimized geometry and here the pair of molecules was taken from the SI of Ref. [26] from a plane-wave DFT optimized structure).

Weights of MEBFs. The weights of the individual contributions of the different MEBFs to the Φ_{1TT} , $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states are listed in Table 2.2. The dominant contributions to the electronic states are highlighted as bold numbers; the Φ_{1TT} state corresponds mainly to the $|\Phi_{1TT}\rangle$ MEBF for the three methodologies.

The AIFDEM predicts a contribution from the $|\Phi_{D-D^+}\rangle$ state that is not observed in the NOCI approach. In order to shed more light on the origin of this discrepancy, we have applied the same shift to NOCI. The NOCI results (Table 2.9) predict also a contribution from $|\Phi_{D_0^+D_0^-}\rangle$ and $|\Phi_{D_0^-D_0^+}\rangle$ after applying the shift. From the shiftings applied to NOCI and AIFDEM, we have observed two opposite trends; in the case of NOCI, the CT states become more important (higher weights) since the CT energies are lowered, whereas in the case of AIFDEM, the CT weights decrease since the CT states are shifted to the reference value which is higher (see Tables 2.9 and 2.10 for shifted and unshifted NOCI and AIFDEM individual weights of MEBFs). For the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states, the main contributions obtained with NOCI and AIFDEM correspond to the $|\Phi_{S_0S_1}\rangle$ and $|\Phi_{S_1S_0}\rangle$ MEBFs, respectively. For the $\Phi_{S_{[1]}}$ state, the configuration $|\Phi_{S_1S_1}\rangle$ was found to have a large weight in the RAS-2SF calculations, however this particular configuration is not of interest for the SF process. The calculated $\Phi_{[2]}$ state with RAS-2SF is dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and it is not included for comparison. In fact, differences in calculated weights with NOCI and AIFDEM and those obtained with RAS-2SF are attributed to the fact that additional configurations, such as $|\Phi_{S_1S_1}\rangle$, are considered in RAS-2SF. In sum, the methods show similar contributions of the different electronic states, despite the differences in the numerical values.

Table 2.2 | Comparison of the individual weights of MEBFs obtained for a pair of tetracene molecules. The main contributions are highlighted as bold numbers. The calculated $\Phi_{[2]}$ state with RAS-2SF is dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and is not included.

State	Φ_{1TT}			$\Phi_{S_{[1]}}$			$\Phi_{S_{[2]}}$		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$ \Phi_{S_0S_0}\rangle$	0.000	0.001	0.000	0.001	0.017	0.002	0.000		0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.001	0.005	0.999	0.642	0.929	0.000		0.009
$ \Phi_{S_1S_0}\rangle$	0.001	0.001	0.027	0.000	0.063	0.016	0.978		0.867
$ \Phi_{1TT}\rangle$	0.999	0.935	0.894	0.000	0.001	0.009	0.020		0.007
$ \Phi_{D^+D^-}\rangle$	0.000	0.008	0.014	0.000	0.023	0.038	0.001		0.112
$ \Phi_{D-D^+}\rangle$	0.000	0.054	0.060	0.000	0.003	0.006	0.000		0.005

Electronic couplings. Electronic couplings between $\Phi_{S[1]}$ and $\Phi_{S[2]}$ with the Φ_{1TT} states calculated with the NOCI approach for the tetracene pair are reported in Table 2.3. In the primed wave functions, the CT states were allowed to mix with the wave functions of the singlet excited and 1TT states. The results indicate that the electronic coupling is enhanced from 2.2 to 37.6 meV when the CT states are allowed to mix; this enhancement is in line with a previous NOCI study of a cluster of three tetracene molecules.[21] A similar trend is observed in the electronic couplings that we calculated with AIFDEM; the values are enhanced when the CT configurations are included in the calculation (see Table 2.11). The increase in the coupling can be then attributed to the mixing in of the CT states with both photo excited states and the excitonic state.

Table 2.3 | Electronic couplings (in meV) between the (diabatic) states $\Phi_{S[1]}$ and $\Phi_{S[2]}$ with Φ_{1TT} for the tetracene pair. In the primed wave functions the CT states were included in the NOCI calculation.

States	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Phi'_{S[1]}$	$\Phi'_{S[2]}$
Φ_{1TT}	4.0	2.2	2.2	58.9
Φ'_{1TT}	7.9	19.6	4.0	37.6

Comparison. All three methods show a similar qualitative trend for the tetracene dimer; they predict that the CT states are too high in energy to be accessed. However, the discrepancies between numerical values are evident. The three methods overestimate the state energies when compared with the experimental values. The NOCI and AIFDEM approaches are conceptually similar. (Static) electron correlation and (local) orbital relaxation effects can be included in the NOCI approach but, at the moment of performing this work, the implementation in the GronOR package was able to treat only small clusters of small molecules. The current AIFDEM implementation is able to handle large clusters and molecules. Additionally, analytical gradients and non-adiabatic couplings are available for the AIFDEM method[26] but not implemented in GronOR so far. Electronic couplings can be directly calculated for NOCI and AIFDEM but for RAS-2SF it is only possible to estimate the coupling based on $||\gamma||^2$ values.

2.3.2. IDENTIFICATION OF A SF MOLECULE BASED ON EXCITATION ENERGIES

In this chapter, a group of SF candidates has been selected and are depicted in Figure 2.2. Vertical excitation energies of the T_1 , S_1 and T_2 states calculated with different levels of electronic structure theories are reported in Table 2.4 together with E_{stt} . SF should be, in principle, an isoergic process which means that E_{stt} must be ideally close to zero. Nevertheless, experimental values (also in Table 2.4) suggest that the process also occurs if it is slightly endo or exoergic. Therefore, for potential SF molecules E_{stt} should lie roughly in the -0.1 to 0.1 eV range. From the results in Table 2.4, molecule **7** or 2-methylene-2H-indene (named as M2I in upcoming discussion) is selected for further evaluation as a promising SF molecule.

Figure 2.2 | Set of potential singlet fission chromophores studied on this chapter.

Table 2.4 | Vertical excitation energies (in eV) of the T_1 , S_1 and T_2 states calculated with different methods for molecules of **1-12**.^a Experimental values; triplet measured in isopentane at 77 K.[33] ^b Experimental results in *n*-heptane.[34] ^{c,d} Measurement in the crystal.[37] ^e In benzene solution.[38] ^f Absorption peak positions in 3-methylpentane at 77 K.[38]

Molecule	Method	$E(T_1)$	$E(S_1)$	$E(T_2)$	E_{stt}^*	Molecule	Method	$E(T_1)$	$E(S_1)$	$E(T_2)$	E_{stt}^*
1	BLYP	1.29	3.19	2.78	0.61	2	BLYP	1.20	2.29	1.94	-0.11
	B3LYP	1.27	3.55	2.94	1.01		B3LYP	1.17	2.74	2.26	0.40
	BHLYP	1.25	3.75	3.06	1.25		BHLYP	1.12	3.44	2.63	1.20
	ω B97X-D	0.91	3.37	2.56	1.55		ω B97X-D	1.16	3.12	2.45	0.80
	SOS-CIS(D)	1.56	3.70	3.48	0.58		SOS-CIS(D)	1.42	3.71	3.02	0.87
	CASPT2	1.36	3.06	3.13	0.34		CASPT2	1.28	3.08	2.71	0.52
	ADC(2)	1.61	3.41	3.46	0.19		ADC(2)	1.47	3.22	2.73	0.28
3	BLYP	1.27	2.72	2.28	0.18	4	BLYP	1.60	2.86	2.61	-0.34
	B3LYP	1.24	3.13	2.53	0.65		B3LYP	1.68	3.55	3.08	0.19
	BHLYP	1.21	3.74	2.79	1.32		BHLYP	1.68	3.65	3.41	-0.07
	ω B97X-D	1.25	3.50	2.70	1.00		ω B97X-D	1.84	3.52	3.34	-0.16
	SOS-CIS(D)	1.52	3.72	3.20	0.68		SOS-CIS(D)	1.97	2.76	3.78	-1.18
	CASPT2	1.34	3.05	2.90	0.37		CASPT2	2.03	2.77	3.59	-1.29
	ADC(2)	1.57	3.79	3.27	0.65		ADC(2)	2.04	2.82	3.52	-1.26
5	BLYP	0.38	0.95	1.93	0.19	6	BLYP	1.57	1.74	2.16	-1.40
	B3LYP	0.45	1.16	1.94	0.26		B3LYP	2.16	2.42	2.60	-1.90
	BHLYP	0.52	1.92	1.48	0.88		BHLYP	2.60	3.23	2.82	-1.97
	ω B97X-D	0.42	1.20	2.22	0.36		ω B97X-D	2.50	2.84	2.71	-2.16
	SOS-CIS(D)	0.87	1.69	2.22	-0.05		SOS-CIS(D)	2.99	3.03	3.70	-2.95
	CASPT2	0.76	1.39	2.26	-0.12		CASPT2	3.00	3.30	4.04	-2.70
	ADC(2)	0.94	1.71	2.40	-0.17		ADC(2)	2.36	2.56	3.06	-2.16
7	BLYP	0.96	1.88	2.56	-0.04	8	BLYP	1.71	2.42	2.27	-1.00
	B3LYP	1.03	2.13	2.57	0.09		B3LYP	1.76	3.20	3.03	-0.32
	BHLYP	1.09	2.47	2.52	0.29		BHLYP	1.75	4.08	4.13	0.58
	ω B97X-D	1.16	2.44	2.65	0.12		ω B97X-D	1.86	3.80	3.62	0.08
	SOS-CIS(D)	1.39	2.63	2.78	-0.15		SOS-CIS(D)	1.94	3.49	4.76	-0.39
	CASPT2	1.30	2.43	2.87	-0.17		CASPT2	1.91	3.31	3.26	-0.51
	ADC(2)	1.30	2.48	2.88	-0.12		ADC(2)	2.03	3.16	3.08	-0.90
9	BLYP	2.01	3.14	3.39	-0.88	10	BLYP	0.94	1.86	2.03	-0.02
	B3LYP	2.07	3.44	3.48	-0.70		B3LYP	0.97	2.15	2.10	0.21
	BHLYP	2.07	3.79	3.46	-0.35		BHLYP	0.96	2.47	2.10	0.55
	ω B97X-D	2.26	3.92	3.63	-0.60		ω B97X-D	1.63	3.19	2.86	-0.07
	SOS-CIS(D)	2.05	3.52	3.66	-0.58		SOS-CIS(D)	1.13	2.54	2.28	0.28
	CASPT2	2.29	3.71	3.83	-0.87		CASPT2	1.77	3.10	3.09	-0.44
	ADC(2)	2.45	3.83	3.93	-1.07		ADC(2)	1.80	3.04	3.05	-0.56
	Experimental	1.84 ^a	3.27 ^b	NA [†]	-0.37		Experimental	1.27 ^a	2.62 ^b	NA [†]	0.08
11	BLYP	1.38	2.39	2.62	-0.37	12	BLYP	1.71	2.90	3.06	-0.52
	B3LYP	1.43	2.68	2.70	-0.18		B3LYP	1.73	3.11	3.24	-0.35
	BHLYP	1.42	3.02	2.70	0.18		BHLYP	1.68	3.32	3.28	-0.04
	ω B97X-D	1.17	2.70	2.26	0.36		ω B97X-D	2.01	3.55	3.53	-0.47
	SOS-CIS(D)	1.49	3.02	3.11	0.04		SOS-CIS(D)	1.60	3.44	3.54	0.24
	CASPT2	1.33	3.17	2.76	0.51		CASPT2	NA [†]	NA [†]	NA [†]	NA [†]
	ADC(2)	1.37	2.80	2.51	0.06		ADC(2)	2.30	3.52	3.84	-1.08
	Experimental	0.86 ^c	1.83 ^d	NA [†]	0.58		Experimental	1.47 ^e	3.01 ^f	3.16 ^e	0.07

* $E_{stt} = E(S_1) - 2E(T_1)$ [†] NA = Not Available

2.3.3. COMPARING NOCI, RAS-2SF AND AIFDEM FOR THE POTENTIAL CHROMOPHORE

Pairs of molecules. In the optimized crystal structure of M2I (see section 2.5), four different pairs of molecules were identified (see Figure 2.3). Two of them show a π -like stacking (slip-stacked) and have been named I-A and I-C, whereas the other two correspond to structural arrangements that differ in the angle between the molecular planes of the molecules, and they are denoted for the upcoming discussion I-B ($\theta = 131^\circ$) and I-D ($\theta = 49^\circ$).

Figure 2.3 | a) Identified pairs of molecules of M2I; from a central molecule (black) the I-A (red), I-B (pink), I-C (green) and I-D (blue) conformations are depicted. b) The angle between the molecular planes in each pair is depicted. Crystal structure optimized at the PBE/6-31G(d,p) level of theory.

Excited state analysis. The first singlet excited and lowest triplet states of M2I correspond mainly to a single excitation with $\pi \rightarrow \pi^*$ character as can be seen from the frontier orbitals depicted in Figure 2.4. The biradicaloid character of M2I has been reported,[39] but a CASSCF(10,10) calculation on the ground state shows 1.83 and 0.20 as the natural orbital occupation numbers for the HOMO and LUMO, respectively, suggesting a closed shell character for the molecule.

Figure 2.4 | Frontier molecular orbitals $2a_2$ and $4b_1$ of 2-methylene-2H-indene taken from the resulting orbitals of a CASSCF(10,10) calculation on the ground state.

Excited state energies. The energies of the Φ_{1TT} , $\Phi_{S_{[1]}}$, $\Phi_{S_{[2]}}$, $\Phi_{D^+D^-}$ and $\Phi_{D^-D^+}$ states for the four pairs of molecules are shown in Table 2.5. The RAS-2SF energies are lower than those obtained with the NOCI approach and the shifted energies in AIFDEM. A close look at the hole and particle contributions in the RAS active space reveals that the HOMO-1 should have been included as an active orbital; the underestimation of the excitation energies in this case suggests that RAS-2SF is suitable for the description of molecules in which it is sufficient to consider the frontier orbitals in the active space, e.g., tetracene. State energies are improved by including the required orbitals in the active space (see RAS(8,6)-2SF and RAS(8,8)-2SF calculations in Table 2.13).

For I-B and I-D, the $\Phi_{[2]}$ state is dominated by the $|\Psi_{S_1S_1}\rangle$ configuration which suggests a double excitation character. Therefore, these states were not included in the comparison. The NOCI energies of the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states are close to the Φ_{1TT} energy deviating by only ~ 0.3 meV, showing that the system almost fulfills the requirement $E_{stt} = 0$. The NOCI $\Phi_{D^+D^-}$ and $\Phi_{D^-D^+}$ energies are 2.0 eV or more above the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ energies indicating that these states are too high in energy to be accessed but might act as virtual states mediating the SF process; the same trend holds for RAS-2SF and AIFDEM CT state energies.

Table 2.5 | State energies (in eV) for the different electronic states for the four pairs of molecules of M2I. For AIFDEM, the unshifted values are shown in parenthesis. $\Phi_{[2]}$ states calculated with RAS-2SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and are not included.

Pair	Method	Φ_{1TT}	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi_{D^+D^-}$	$\Phi_{D^-D^+}$
I-A	NOCI	2.15	2.47	2.49	4.27	4.32
	RAS(4,4)-2SF	1.33	1.97	2.08	3.29	3.32
	AIFDEM	2.29(3.38)	2.43(3.53)	2.50(4.05)	5.03(2.68)	5.13(2.99)
I-B	NOCI	2.12	2.41	2.42	4.69	5.07
	RAS(4,4)-2SF	1.28	1.96		4.05	
	AIFDEM	2.33(2.95)	2.39(3.02)	2.53(3.17)	5.00(2.78)	5.11(3.11)
I-C	NOCI	2.12	2.41	2.42	4.69	5.07
	RAS(4,4)-2SF	1.27	1.96	1.98	4.11	4.25
	AIFDEM	2.34(2.72)	2.41(3.02)	2.47(3.07)	5.00(2.92)	5.12(2.94)
I-D	NOCI	2.11	2.39	2.42	4.36	4.92
	RAS(4,4)-2SF	1.26	1.97		3.64	
	AIFDEM	2.33(2.97)	2.43(3.01)	2.46(3.19)	5.00(2.40)	5.12(2.90)

Weights of MEBFs. Table 2.6 shows a comparison between the weights of the MEBFs to the Φ_{1TT} , $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states in the pairs of molecules. The dominant contributions, highlighted as bold numbers, show that for the four pairs of molecules the Φ_{1TT} states have almost pure $|\Phi_{1TT}\rangle$ character, whereas $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ are described mainly by the singlet excited MEBFs; the weights suggest that the excitation is localized on one of the two molecules for all the cases. A similar trend is observed with the RAS-2SF and AIFDEM methodologies, although in RAS-2SF the $|C|^2$ values are lower than those calculated with NOCI and AIFDEM since additional configurations, such as double excitations ($|\Phi_{S_1S_1}\rangle$), contribute. NOCI shows that the states in I-B, I-C and I-D retain mostly a pure character, which is also observed in the individual contributions calculated with RAS-2SF and

AIFDEM. However, the contributions for the Φ_{1TT} state in dimer I-A are different between the methods; the weights from the NOCI calculation predict that Φ_{1TT} has mainly a contribution from the $|\Phi_{1TT}\rangle$ MEBF with a small contribution from $|\Phi_{S_0S_1}\rangle$, whereas RAS-2SF and the weights obtained with AIFDEM predict a contribution from the CT states. After applying the same shift to NOCI, contributions from the CT states are also observed (see Table 2.14). When we shift NOCI and AIFDEM (see Tables 2.14 and 2.15), we observed the same trends in the weights as in tetracene.

Table 2.6 | Comparison of the individual weights of MEBFs in the four pair arrangements of M2I. The main contributions are highlighted as bold numbers. $\Phi_{[2]}$ states calculated with RAS-2SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and are not included.

Pair I-A									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$ \Phi_{S_0S_0}\rangle$	0.001	0.001	0.000	0.000	0.066	0.014	0.000	0.000	0.007
$ \Phi_{S_0S_1}\rangle$	0.014	0.013	0.041	0.982	0.665	0.889	0.000	0.000	0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.013	0.059	0.000	0.000	0.000	0.999	0.828	0.929
$ \Phi_{1TT}\rangle$	0.985	0.885	0.539	0.018	0.060	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.037	0.000	0.000	0.019	0.096	0.000	0.008	0.063
$ \Phi_{D^-D^+}\rangle$	0.000	0.037	0.360	0.000	0.019	0.000	0.000	0.008	0.000
Pair I-B									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.009	0.001	0.000		0.004
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.001	1.000	0.675	0.995	0.000		0.003
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.003	1.000		0.991
$ \Phi_{1TT}\rangle$	1.000	1.000	0.999	0.000	0.000	0.000	0.000		0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.001	0.000		0.002
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.000
Pair I-C									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.015	0.001
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.000	1.000	0.853	0.996	0.000	0.000	0.003
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.003	1.000	0.822	0.996
$ \Phi_{1TT}\rangle$	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pair I-D									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.226	0.001	0.000		0.001
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.000	1.000	0.572	0.999	0.000		0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	1.000		0.999
$ \Phi_{1TT}\rangle$	1.000	0.996	0.998	0.000	0.000	0.000	0.000		0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.003	0.001	0.000	0.004	0.000	0.000		0.000
$ \Phi_{D^-D^+}\rangle$	0.000	0.001	0.001	0.000	0.002	0.000	0.000		0.000

Electronic couplings. In Table 2.7, electronic couplings are reported for the four pairs of molecules between the $\Phi_{S[1]}$ and $\Phi_{S[2]}$ states with the Φ_{1TT} state. The largest coupling values are observed in I-A, whereas the lower values are obtained for I-B and I-C. For I-A, the inclusion of the CT states to the $\Phi_{S[1]}$ state enhances the electronic coupling from 21.4 to 42.2 meV. The electronic coupling is also enhanced if the CT states are allowed to interact only with the Φ_{1TT} state. For the $\Phi_{S[2]}$ state, no significant enhancement is observed. The most plausible determination of the electronic coupling in I-A corresponds to that in which the CT states are allowed to mix with both the $\Phi_{S[1]}$ and Φ_{1TT} states, with a value of 39.8 meV.

Table 2.7 | Electronic couplings (in meV) between the (diabatic) states $\Phi_{S[1]}$ and $\Phi_{S[2]}$ with Φ_{1TT} for the dimer arrangements of M2I. In the primed wave functions the CT states were included in the NOCI calculation.

Pair	States	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Phi'_{S[1]}$	$\Phi'_{S[2]}$
I-A	Φ_{1TT}	21.4	0.4	42.2	0.4
I-B		0.2	0.1	0.2	0.2
I-C		0.0	0.3	0.0	0.4
I-D		0.6	0.6	0.4	1.3
I-A	Φ'_{1TT}	38.0	1.1	39.8	0.4
I-B		0.2	0.3	0.2	0.2
I-C		0.0	0.4	0.0	0.4
I-D		0.1	1.2	0.3	1.3

The magnitude of the electronic coupling suggests that the formation of the 1TT state could occur efficiently. We performed the same analysis for the four pairs of molecules in which the molecules were replaced by optimized molecules (Tables 2.16, 2.17 and 2.18). Originally, the pairs of molecules from the periodic DFT optimization were slightly bent, and after the replacement they became planar. Although the quantitative results changed, the same observations as discussed above (regarding the excitation energies of the states, the individual contributions of the MEBFs and the electronic couplings) are observed; the highest electronic coupling is found for I-A and the lowest for I-B and I-C. It is apparent that the electronic couplings strongly depend on the orientation of the molecules in the cluster.

Table 2.8 shows the configurational analysis of the RAS-2SF wave functions of the pairs of molecules showing their local excited (LE), multi excitonic (ME) and CT character, and the $||\gamma||^2$ values between the Φ_{1TT} with $\Phi_{S[1]}$ and $\Phi_{S[2]}$ states are also listed. The $||\gamma||^2$ values indicate that the transition is most probable to occur when the molecules are disposed as in arrangement I-A (0.25 and 0.30), for I-D also a transition is expected to occur (0.09), whereas for I-B and I-C no transition would be observed. The $||\gamma||^2$ values obtained with the RAS(8,6)-2SF and RAS(8,8)-2SF calculations (see Tables 2.19 and 2.20) show the same trend. The differences in the $||\gamma||^2$ values can be associated to the degree of contribution of the CT states to the singlet excited and 1TT states. CT contributions are predicted for I-A and I-D whereas they are negligible for I-B and I-C. Remarkably, the electronic couplings calculated with NOCI and AIFDEM (Table 2.21) follow the qualitative behaviour predicted by the RAS-2SF method, in which the highest values are observed for

I-A; this implies that if the molecules are disposed as in this conformation in the crystal structure, the SF process might occur efficiently.

Table 2.8 | Configuration analysis of the RAS-2SF wave functions for the pair arrangements of M2I using localized orbitals within the DMO-LCFMO framework. The values of $||\gamma||^2$ between the Φ_{1TT} and each of the local excited states $\Phi_{S[1]}$ and $\Phi_{S[2]}$ are shown. $\Phi_{[2]}$ states calculated with RAS-2SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration, and are not included for comparison.

Pair	State	LE	ME	CT	$ \gamma ^2$	Pair	State	LE	ME	CT	$ \gamma ^2$
I-A	Φ_{1TT}	0.03	0.89	0.07		I-B	Φ_{1TT}	0.00	1.00	0.00	
	$\Phi_{S[1]}$	0.83	0.15	0.02	0.25		$\Phi_{S[1]}$	0.67	0.32	0.00	0.01
	$\Phi_{S[2]}$	0.66	0.23	0.04	0.30		$\Phi_{S[2]}$				
I-C	Φ_{1TT}	0.00	1.00	0.00		I-D	Φ_{1TT}	0.00	0.99	0.00	
	$\Phi_{S[1]}$	0.85	0.15	0.00	0.02		$\Phi_{S[1]}$	0.57	0.20	0.01	0.09
	$\Phi_{S[2]}$	0.82	0.16	0.00	0.02		$\Phi_{S[2]}$				

2.4. CONCLUSIONS

We report a comparison of the NOCI approach with two theoretical approaches, RAS-2SF and AIFDEM used for the study of SF, and we propose 2-methylene-2H-indene as a potential SF molecule.

The comparison of the methods indicate that for tetracene, NOCI, RAS-2SF and AIFDEM overestimate the energies of the states when compared with the experimental values. Despite this overestimation, our results suggest that the CT states act as virtual states in the SF process. The three methods agree on the character of the excited states, however, more configurations were found to be important in the RAS-2SF calculations, which were not included in the NOCI and AIFDEM calculations. The major difference between the NOCI and AIFDEM approaches, despite being conceptually similar, are that electron correlation and orbital relaxation effects can be included in the NOCI approach, but at the moment only small clusters of small molecules can be treated, whereas the AIFDEM approach can handle large clusters and molecules.

Calculated electronic couplings for four pairs of the 2-methylene-2H-indene with the NOCI and AIFDEM approaches, and $||\gamma||^2$ values calculated with RAS-2SF show that the formation of the 1TT state could occur efficiently in the crystal when the molecules are oriented as in conformation I-A. NOCI and AIFDEM overestimate the state energies, whereas RAS-2SF underestimates them; however, the three methods predict similar character for the relevant electronic states. The CT state energies are too high to be accessible, and a mediated mechanism is proposed for the SF process in 2-methylene-2H-indene.

Finally, the methodologies are able to distinguish between configurations with low and high SF probabilities. A further comparison beyond these two systems has to be done in order to establish and generalize the predictive power of the methodologies. Additionally, the findings of this chapter open new lines of research on the derivatives of the M2I chromophore for further theoretical investigations as potential SF candidates.

2.5. COMPUTATIONAL DETAILS

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The identification of suitable SF molecules requires the evaluation of excitation energies. T_1 , S_1 and T_2 (vertical) excitation energies for a set of candidates (Figure 2.2) were calculated with various methodologies. TD-DFT, SOS-CIS(D) and ADC(2) calculations were performed using Q-Chem 5.0,[40] whereas the CASSCF/CASPT2 calculations with the MOLCAS 8.0[41] code. The active spaces selected for each of the molecules are specified in Table 2.12. Unless otherwise stated, the basis set used is cc-pVDZ.

A crystal structure of the potential SF molecule is proposed: the crystal structure of **7** was optimised using periodic DFT calculations at the PBE/6-31G(d,p) level of theory. Both the atom positions and cell parameters were optimized using a $4 \times 4 \times 4$ k-point mesh, followed by a frequency calculation showing that the crystal structure corresponds to a genuine minimum. In addition, the Grimme dispersion correction was included for the optimizations. All of these calculations were performed using the CRYSTAL14[47] *ab initio* package. To the best of our knowledge the crystal structure of **7** has not been reported so far, therefore a possible crystal structure has been obtained by performing periodic DFT calculations starting from the known crystal structure of the analogue compound 2-(dicyanomethylene)indene-1,3-dione. The optimization of **7** led to a genuine minimum (confirmed by a frequency calculation) that shows $P2_1/c$ as the space group with the following final cell parameters: $a = 8.693 \text{ \AA}$, $b = 10.316 \text{ \AA}$, $c = 7.491 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 102.96^\circ$ and $\gamma = 90^\circ$. The volume of the unit cell is $654.65 \text{ \AA}^3$ and the density is $1.299 \text{ g} \cdot \text{cm}^{-3}$. Additionally, the molecules in the identified pairs in the optimized crystal structure were replaced by an optimized molecule at the ω B97X-D/cc-pVDZ level of theory, by arranging them as in the respective crystal structure distance and angle. Electronic couplings were calculated for the pairs of molecules obtained by the periodic DFT calculations and for the pairs in which the molecules were replaced, in order to study the influence of different structural arrangements in the electronic couplings.

Molecular wave functions of the CASSCF-type with an active space of four electrons in four orbitals (CASSCF(4,4)) describing the S_0 , S_1 , T_1 , D_0^+ and D_0^- states for the different molecules in each pair were calculated using the Gamess-UK package.[42] MEBFs representing the following electronic states of the pairs of molecules were generated: $|\Phi_{S_0 S_0}\rangle$, $|\Phi_{S_1 S_0}\rangle$, $|\Phi_{S_0 S_1}\rangle$, $|\Phi_{1 TT}\rangle$, $|\Phi_{D_0^+ D_0^-}\rangle$ and $|\Phi_{D_0^- D_0^+}\rangle$. Two diabatic states, $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ were constructed from a 2×2 NOCI calculation in the basis of the $|\Phi_{S_0 S_1}\rangle$ and $|\Phi_{S_1 S_0}\rangle$ MEBFs, whereas the diabatic state $\Phi_{1 TT}$ corresponds to the $|\Phi_{1 TT}\rangle$ MEBF. The influence of the CT states is explored by adding the corresponding MEBFs to the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states (resulting in 4×4 NOCI calculations) and to the $\Phi_{1 TT}$ (resulting in a 3×3 NOCI calculation). To investigate the importance of each MEBF in the diabatic $\Phi_{S_{[1]}}$, $\Phi_{S_{[2]}}$ and $\Phi_{1 TT}$ states, the weights (ω_i) of the MEBFs were calculated using the Gallup and Norbeck scheme,[43] $\omega_i = |C_i|^2 / (S^{-1})_{ii}$, where C_i corresponds to the CI coefficient of the i^{th} MEBF and $(S^{-1})_{ii}$ denotes the ii^{th} element of the inverse of the overlap matrix in the MEBF basis. The NOCI methodology has been implemented in the package GronOR.[44] The calculation of the Hamiltonian matrix elements is performed by means of the factorized cofactor method which is described in Ref. [45].

2.6. APPENDIX

2.6.1. CALCULATED WEIGHTS WHEN NOCI AND AIFDEM ARE SHIFTED FOR THE TETRACENE MOLECULE

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Table 2.9 | Comparison of the individual weights of MEBFs obtained with NOCI (shifted and unshifted) in tetracene dimer. The main contributions are highlighted as bold numbers. s=shifted and u=unshifted.

State →	Φ_{1TT}		$\Phi_{S[1]}$		$\Phi_{S[2]}$	
Configuration	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.001	0.002	0.000	0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.999	0.978	0.000	0.001
$ \Phi_{S_1S_0}\rangle$	0.001	0.000	0.000	0.000	0.978	0.879
$ \Phi_{1TT}\rangle$	0.999	0.962	0.000	0.013	0.021	0.007
$ \Phi_{D^+D^-}\rangle$	0.000	0.002	0.000	0.000	0.001	0.005
$ \Phi_{D^-D^+}\rangle$	0.000	0.036	0.000	0.007	0.000	0.112

Table 2.10 | Comparison of the individual weights of MEBFs obtained with AIFDEM (shifted and unshifted) in tetracene dimer. The main contributions are highlighted as bold numbers. s=shifted and u=unshifted.

State →	Φ_{1TT}		$\Phi_{S[1]}$		$\Phi_{S[2]}$	
Configuration	AIFDEM (u)	AIFDEM (s)	AIFDEM (u)	AIFDEM (s)	AIFDEM(u)	AIFDEM (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.002	0.002	0.000	0.000
$ \Phi_{S_0S_1}\rangle$	0.001	0.005	0.831	0.929	0.000	0.009
$ \Phi_{S_1S_0}\rangle$	0.008	0.027	0.032	0.016	0.705	0.867
$ \Phi_{1TT}\rangle$	0.875	0.894	0.007	0.009	0.012	0.007
$ \Phi_{D^+D^-}\rangle$	0.006	0.014	0.090	0.038	0.265	0.112
$ \Phi_{D^-D^+}\rangle$	0.110	0.060	0.038	0.006	0.017	0.005

2.6.2. ADDITIONAL CALCULATION OF ELECTRONIC COUPLINGS IN TETRACENE

Electronic couplings calculated with the AIFDEM methodology are shown in Table 2.11. The results are in the meV range, which is in agreement with previously reported electronic couplings for a tetracene trimer[21] and those calculated in our work. The values are enhanced when the charge transfer configurations are allowed to mix with the singlet and 1TT states; they increase an order of magnitude.

Table 2.11 | AIFDEM electronic couplings (in meV) between the diabatic states $\Phi_{S[1]}$ and $\Phi_{S[2]}$ with Φ_{1TT} for the tetracene dimer. In the primed wave functions the charge transfer states were included.

States	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Phi'_{S[1]}$	$\Phi'_{S[2]}$
Φ_{1TT}	5.1	0.6	10.0	7.8
Φ'_{1TT}	9.5	36.3	13.4	18.6

2.6.3. EXCITATION ENERGIES OF THE PROPOSED CANDIDATES

Table 2.4 collects the vertical excitation energies, in eV, for the potential chromophores depicted in Figure 2.2 using different methods.

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We performed a comparison of the excitation energies using different levels of theory ranging from single to multi reference methods in order to determine a plausible singlet fission molecule. Due to the large active space required, CASSCF/CASPT2 calculations on **12** were not performed. The ω B97X-D values for most cases are relatively close to the CASSCF/CASPT2 and ADC(2) values. This is in agreement with a previously reported benchmarking study,[30] in which they have shown that the ω B97X-D functional gives the best description of exciton properties when compared with high-level wave function-based methods.

One observes the typical blue-shift of all states to higher excitation energies when the fraction of Hartree-Fock (HF) exchange is increased from zero (BLYP) to 20% (B3LYP), and finally to 50% (BHLYP), but the order of states remains essentially the same. We have also calculated the singlet and triplet vertical excitation energies of the optimized monomers using ω B97X-D functional since the corresponding energies are used as reference values for shifting in the AIFDEM and NOCI methodologies. We have extended the calculations further to single reference, SOS-CIS(D) and ADC(2) and multi reference, CASSCF/CASPT2, wave function based methods. The excitation energies are typically overestimated when compared to the experimental values, and this can be attributed to the fact that the calculations were performed in the gas phase and the experimental values were measured either in solution or in the crystal structure, but also to the fact that vibrational effects are neglected. Calculation of the 0-0 transitions for tetracene show that the S_1 0-0 excitation is 2.63 eV, and for the T_1 0-0 excitation is 1.32 eV. Remarkably, the ADC(2) energies for most of the cases are close to the corresponding CASSCF/CASPT2 values, being ADC(2) computationally less demanding than the multi reference CASSCF/CASPT2 method. SOS-CIS(D) energies are in line with ADC(2) and CASSCF/CASPT2 values and in most cases closer to experimental values, mostly due to the fact that CIS(D) energies are semi-empirically improved. It must be noted that SOS-CIS(D) energy can be evaluated with the fourth power of the molecular size by adopting Laplace transform technique and can be applied to the calculations of excitation energies for relatively large molecules.

2.6.4. SELECTED ACTIVE SPACES FOR THE SET OF CANDIDATES

Table 2.12 shows the active spaces selected for the CASSCF/CASPT2 calculations. Orbitals that were not included in the active space are mentioned in Notes.

Table 2.12 | Selected active spaces for the set of candidates. Notes are included for clarification of the active spaces.

Molecule	Active Space Selected	Notes
1	CASSCF(16,16)	π -out-of-plane orbitals in the -CN group were not included
2	CASSCF(16,16)	π -out-of-plane orbitals in the -CN group were not included
3	CASSCF(16,16)	π -out-of-plane orbitals in the -CN group were not included
4	CASSCF(14,14)	π -out-of-plane orbitals in the -CN group were not included
5	CASSCF(14,14)	π -out-of-plane orbitals in the -CN group were not included
6	CASSCF(16,16)	π -out-of-plane orbitals in the -CN group were not included
7	CASSCF(10,10)	π -out-of-plane orbitals in the -CN group were not included
8	CASSCF(8,6)	
9	CASSCF(4,4)	
10	CASSCF(4,4)	
11	CASSCF(4,4)	
12	Not performed	

2.6.5. RAS(8,6)-2SF AND RAS(8,8)-2SF STATE ENERGIES

Table 2.13 | State energies (in eV) for the different electronic states for the four pairs of 7.

Dimer	Method	Φ_{1TT}	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi_{D^+D^-}$	$\Phi_{D^-D^+}$
I-A	RAS(8,6)-2SF	1.75	2.05	2.11	3.23	3.28
	RAS(8,8)-2SF	1.69	2.08	2.15	3.19	3.25
I-B	RAS(8,6)-2SF	1.87	2.02		4.18	
	RAS(8,8)-2SF	1.79	2.08		4.13	
I-C	RAS(8,6)-2SF	1.86	2.03	2.04	4.73	4.73
	RAS(8,8)-2SF	1.78	2.09	2.11	4.71	4.71
I-D	RAS(8,6)-2SF	1.85	2.04		3.72	
	RAS(8,8)-2SF	1.77	2.10		3.68	

$\Phi_{[2]}$ states calculated with RAS-SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and are not included for comparison.

2.6.6. CALCULATED WEIGHTS WHEN NOCI AND AIFDEM ARE SHIFTED FOR 2-METHYLENE-2H-INDENE

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Table 2.14 | Comparison of the individual weights of MEBFs obtained with NOCI (shifted and unshifted) in pairs of 7. The main contributions are highlighted as bold numbers. s=shifted and u=unshifted.

Dimer I-A						
State →	Φ_{1TT}		$\Phi_{S[1]}$		$\Phi_{S[2]}$	
Configuration	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)
$ \Phi_{S_0S_0}\rangle$	0.001	0.000	0.000	0.000	0.000	0.000
$ \Phi_{S_0S_1}\rangle$	0.014	0.008	0.982	0.989	0.001	0.002
$ \Phi_{S_1S_0}\rangle$	0.000	0.002	0.000	0.001	0.999	0.994
$ \Phi_{1TT}\rangle$	0.985	0.983	0.018	0.008	0.000	0.002
$ \Phi_{D^+D^-}\rangle$	0.000	0.004	0.000	0.001	0.000	0.001
$ \Phi_{D^-D^+}\rangle$	0.000	0.003	0.000	0.001	0.000	0.001

Dimer I-B						
State →	Φ_{1TT}		$\Phi_{S[1]}$		$\Phi_{S[2]}$	
Configuration	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	1.000	0.999	0.000	0.001
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.001	1.000	0.999
$ \Phi_{1TT}\rangle$	1.000	1.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000

Dimer I-C						
State →	Φ_{1TT}		$\Phi_{S[1]}$		$\Phi_{S[2]}$	
Configuration	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	1.000	1.000	0.000	0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	1.000	1.000
$ \Phi_{1TT}\rangle$	1.000	1.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000

Dimer I-D						
State →	Φ_{1TT}		$\Phi_{S[1]}$		$\Phi_{S[2]}$	
Configuration	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)	NOCI(u)	NOCI (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	1.000	0.994	0.000	0.004
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.004	1.000	0.994
$ \Phi_{1TT}\rangle$	1.000	1.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.000	0.001	0.000	0.001
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.001	0.000	0.001

Table 2.15 | Comparison of the individual weights of MEBFs obtained with AIFDEM (shifted and unshifted) in pairs of 7. The main contributions are highlighted as bold numbers. s=shifted and u=unshifted.

Dimer I-A						
State →	$\Phi_{1\,TT}$		$\Phi_{S_{[1]}}$		$\Phi_{S_{[2]}}$	
Configuration	AIFDEM (u)	AIFDEM (s)	AIFDEM (u)	AIFDEM (s)	AIFDEM(u)	AIFDEM (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.014	0.009	0.007	0.000
$ \Phi_{S_0S_1}\rangle$	0.041	0.059	0.889	0.879	0.000	0.000
$ \Phi_{S_1S_0}\rangle$	0.059	0.037	0.000	0.000	0.929	0.995
$ \Phi_{1\,TT}\rangle$	0.539	0.880	0.000	0.105	0.000	0.001
$ \Phi_{D^+D^-}\rangle$	0.000	0.013	0.096	0.004	0.063	0.004
$ \Phi_{D^-D^+}\rangle$	0.360	0.011	0.000	0.003	0.000	0.000

Dimer I-B						
State →	$\Phi_{1\,TT}$		$\Phi_{S_{[1]}}$		$\Phi_{S_{[2]}}$	
Configuration	AIFDEM (u)	AIFDEM (s)	AIFDEM (u)	AIFDEM (s)	AIFDEM(u)	AIFDEM (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.001	0.002	0.004	0.002
$ \Phi_{S_0S_1}\rangle$	0.001	0.000	0.995	0.998	0.003	0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.003	0.000	0.991	0.998
$ \Phi_{1\,TT}\rangle$	0.999	1.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.001	0.000	0.002	0.000
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000

Dimer I-C						
State →	$\Phi_{1\,TT}$		$\Phi_{S_{[1]}}$		$\Phi_{S_{[2]}}$	
Configuration	AIFDEM (u)	AIFDEM (s)	AIFDEM (u)	AIFDEM (s)	AIFDEM(u)	AIFDEM (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.001	0.001	0.001	0.002
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.996	0.999	0.003	0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.003	0.000	0.996	0.998
$ \Phi_{1\,TT}\rangle$	1.000	1.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D^-D^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000

Dimer I-D						
State →	$\Phi_{1\,TT}$		$\Phi_{S_{[1]}}$		$\Phi_{S_{[2]}}$	
Configuration	AIFDEM (u)	AIFDEM (s)	AIFDEM (u)	AIFDEM (s)	AIFDEM(u)	AIFDEM (s)
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.001	0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.999	0.998	0.000	0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.999	0.996
$ \Phi_{1\,TT}\rangle$	0.998	1.000	0.000	0.000	0.000	0.000
$ \Phi_{D^+D^-}\rangle$	0.001	0.000	0.000	0.001	0.000	0.002
$ \Phi_{D^-D^+}\rangle$	0.001	0.000	0.000	0.001	0.000	0.002

2.6.7. RESULTS AND ANALYSIS OF DIMERS IN WHICH MONOMERS WERE REPLACED

Table 2.16 shows the relative energies of the different electronic states of interest. The energy values correspond to the dimers in which the monomers have been replaced by optimised monomers; they show a similar trend in which the charge transfer state energies are higher than the $\Phi_{1\,TT}$, $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states suggesting that the CT states act as virtual states in a mediated transition.

The electronic couplings for the dimers in which the monomers were replaced are reported in Table 2.17. Although the numerical values have changed, they show the same qualitative behaviour in which the highest value corresponds to dimer I-A and in a lesser

Table 2.16 | Relative energies (in eV) of the Φ_{1TT} , $\Phi_{S[1]}$, $\Phi_{S[2]}$, $\Phi_{D^+D^-}$ and $\Phi_{D^-D^+}$ states obtained with the different methodologies.

Dimer	Method	Φ_{1TT}	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Phi_{D^+D^-}$	$\Phi_{D^-D^+}$
I-A	NOCI	2.99	3.03	3.06	4.77	4.82
	RAS(4,4)-2SF	2.07	2.45	2.56	3.70	3.80
	AIFDEM	2.29	2.43	2.50	5.03	5.13
I-B	NOCI	3.01	2.96	2.97	5.54	5.54
	RAS(4,4)-2SF	2.00	2.43		4.45	4.96
	AIFDEM	2.29	2.43	2.50	5.03	5.13
I-C	NOCI	3.01	2.96	2.97	5.54	5.54
	RAS(4,4)-2SF	2.01	2.44	2.46	4.96	4.97
	AIFDEM	2.29	2.43	2.50	5.03	5.13
I-D	NOCI	2.95	2.98	3.01	4.86	5.34
	RAS(4,4)-2SF	2.00	2.40		4.60	4.79
	AIFDEM	2.29	2.43	2.50	5.03	5.13

extent in dimer I-D, whereas for I-B and I-C the electronic coupling values are close to zero.

Table 2.17 | Electronic couplings (in meV) between the diabatic states $\Phi_{S[1]}$ and $\Phi_{S[2]}$ with Φ_{1TT} for the dimer arrangements of **7**. In the primed wave functions the charge transfer states were included in the NOCI calculation.

Dimer	States	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Phi'_{S[1]}$	$\Phi'_{S[2]}$
I-A	Φ_{1TT}	10.4	5.9	21.3	8.2
I-B		0.0	0.4	0.0	0.7
I-C		0.0	0.4	0.0	0.7
I-D		0.5	0.0	2.1	0.1
I-A	Φ'_{1TT}	20.8	9.8	21.2	8.1
I-B		0.0	0.7	0.0	0.6
I-C		0.0	0.7	0.0	0.7
I-D		2.3	0.1	2.4	0.1

Table 2.18 reports the weights of the individual MEBFs in the Φ_{1TT} , $\Phi_{S[1]}$ and $\Phi_{S[2]}$ states; the main contributions are highlighted as bold numbers. The results show a similar trend to those obtained with the dimers extracted from the optimised crystal structure.

Table 2.18 | Comparison of the weights of the MEBFs obtained with the methodologies in the four dimer arrangements of **7**. For the case of NOCI and AIFDEM, the weights of individual MEBFs are shown. For RAS-2SF the square of the amplitudes are listed. The main contributions are highlighted as bold numbers.

Dimer I-A									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$\Phi_{S_0S_0}$	0.000	0.003	0.006	0.000	0.061	0.010	0.000	0.001	0.000
$\Phi_{S_0S_1}$	0.126	0.015	0.186	0.848	0.704	0.954	0.033	0.000	0.002
$\Phi_{S_1S_0}$	0.076	0.012	0.003	0.007	0.000	0.004	0.918	0.860	0.997
Φ_{1TT}	0.780	0.918	0.463	0.146	0.051	0.000	0.049	0.000	0.000
$\Phi_{D^+D^-}$	0.000	0.020	0.012	0.000	0.016	0.031	0.000	0.004	0.000
$\Phi_{D^-D^+}$	0.000	0.030	0.331	0.000	0.016	0.001	0.000	0.004	0.000
Dimer I-B									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$\Phi_{S_0S_0}$	0.000	0.000	0.000	0.000	0.002	0.000	0.000		0.000
$\Phi_{S_0S_1}$	0.000	0.000	0.034	1.000	0.699	1.000	0.000		0.000
$\Phi_{S_1S_0}$	0.000	0.000	0.000	0.000	0.000	0.000	1.000		1.000
Φ_{1TT}	1.000	1.000	0.964	0.000	0.000	0.000	0.000		0.000
$\Phi_{D^+D^-}$	0.000	0.000	0.002	0.000	0.000	0.000	0.000		0.000
$\Phi_{D^-D^+}$	0.000	0.000	0.000	0.000	0.001	0.000	0.000		0.000
Dimer I-C									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$\Phi_{S_0S_0}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.026	0.000
$\Phi_{S_0S_1}$	0.000	0.000	0.000	1.000	0.882	1.000	0.000	0.000	0.000
$\Phi_{S_1S_0}$	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.828	0.998
Φ_{1TT}	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000
$\Phi_{D^+D^-}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
$\Phi_{D^-D^+}$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dimer I-D									
	Φ_{1TT}			Φ_{S_1}			Φ_{S_2}		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$\Phi_{S_0S_0}$	0.000	0.000	0.000	0.000	0.151	0.000	0.000		0.000
$\Phi_{S_0S_1}$	0.000	0.000	0.172	1.000	0.483	0.999	0.000		0.000
$\Phi_{S_1S_0}$	0.000	0.000	0.000	0.000	0.000	0.001	1.000		1.000
Φ_{1TT}	1.000	0.996	0.826	0.000	0.000	0.000	0.000		0.000
$\Phi_{D^+D^-}$	0.000	0.003	0.000	0.000	0.005	0.000	0.000		0.000
$\Phi_{D^-D^+}$	0.000	0.001	0.002	0.000	0.002	0.000	0.000		0.000

2.6.8. ADDITIONAL RAS-2SF CALCULATIONS WITH LARGER ACTIVE SPACES

Tables 2.19 and 2.20 show the configuration analysis of the RAS(8,6)-2SF and RAS(8,8)-2SF wave functions for the dimers of **7** using localized orbitals within the DMO-LCFMO framework.[48, 49] The values of $||\gamma||^2$ are also listed for the transition between the Φ_{1TT} with the Φ_{S_1} and Φ_{S_2} states.

Electronic couplings calculated with the AIFDEM methodology for the four dimers of **7** are shown in Table 2.21. The results follow the same trend in which the highest value is observed for dimer I-A and the lowest ones correspond to dimers I-B and I-C.

Table 2.19 | Configuration analysis of the RAS-2SF wave functions for the dimer arrangements in the crystal structure of **7** using localized orbitals within the DMO-LCFMO framework. The values of $||\gamma||^2$ between the Φ_{1TT} and each of the local excited states Φ_{S_1} and Φ_{S_2} are shown.

RAS(8,6)-2SF											
Dimer	State	LE	ME	CR	$ \gamma ^2$	Dimer	State	LE	ME	CR	$ \gamma ^2$
I-A	Φ_{1TT}	0.17	0.70	0.11		I-B	Φ_{1TT}	0.00	1.00	0.00	
	Φ_{S_1}	0.58	0.37	0.02	0.12		Φ_{S_1}	0.74	0.24	0.00	0.00
	Φ_{S_2}	0.85	0.13	0.03	0.17		Φ_{S_2}				
I-C	Φ_{1TT}	0.00	1.00	0.00		I-D	Φ_{1TT}	0.00	0.99	0.01	
	Φ_{S_1}	0.68	0.32	0.00	0.00		Φ_{S_1}	0.61	0.19	0.01	0.01
	Φ_{S_2}	0.66	0.33	0.00	0.00		Φ_{S_2}				

Table 2.20 | Configuration analysis of the RAS-2SF wave functions for the dimer arrangements in the crystal structure of **7** using localized orbitals within the DMO-LCFMO framework. The values of $||\gamma||^2$ between the Φ_{1TT} and each of the local excited states Φ_{S_1} and Φ_{S_2} are shown.

RAS(8,8)-2SF											
Dimer	State	LE	ME	CR	$ \gamma ^2$	Dimer	State	LE	ME	CR	$ \gamma ^2$
I-A	Φ_{1TT}	0.10	0.77	0.13		I-B	Φ_{1TT}	0.00	1.00	0.00	
	Φ_{S_1}	0.62	0.29	0.05	0.10		Φ_{S_1}	0.71	0.27	0.00	0.00
	Φ_{S_2}	0.82	0.14	0.05	0.12		Φ_{S_2}				
I-C	Φ_{1TT}	0.00	1.00	0.00		I-D	Φ_{1TT}	0.00	0.99	0.01	
	Φ_{S_1}	0.66	0.34	0.00	0.00		Φ_{S_1}	0.61	0.20	0.01	0.01
	Φ_{S_2}	0.64	0.35	0.00	0.00		Φ_{S_2}				

Table 2.21 | Electronic couplings (in meV) between the diabatic states $\Phi_{S[1]}$ and $\Phi_{S[2]}$ with Φ_{1TT} for the dimer arrangements of **7** calculated with the AIFDEM methodology. In the primed wave functions the charge transfer states were included.

Dimer	States	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Phi'_{S[1]}$	$\Phi'_{S[2]}$
I-A	Φ_{1TT}	33.4	12.1	180.2	118.4
I-B		0.6	2.0	2.6	1.2
I-C		0.0	0.0	2.9	0.0
I-D		0.6	2.7	0.7	5.4
I-A	Φ'_{1TT}	95.2	34.3	119.0	85.3
I-B		2.1	2.0	2.3	1.6
I-C		0.0	0.0	1.2	0.0
I-D		12.5	31.2	0.3	10.1

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3

A COMPARISON OF ELECTRONIC COUPLINGS WITH A FRONTIER ORBITAL APPROACH AND *ab initio* CALCULATIONS

V_{SIMPLE}^2 vs. $V_{ab\ INITIO}^2$?

Based on J. L. Ryerson, A. Zaykov, L. E. Aguilar Suarez, R. W. A. Havenith, B. R. Stepp, P. I. Dron, J. Kaleta, A. Akdag, S. J. Teat, T. F. Magnera, J. R. Miller, Z. Havlas, R. Broer, S. Faraji, J. Michl, J. C. Johnson *Structure and photophysics of indigoids for singlet fission: Cibacalcrot*. J. Chem. Phys. **2019**, 151, 184903.

ABSTRACT

Finding new singlet fission (SF) materials is an active area of research. Once a chromophore has been identified to fulfil the energetic criteria of SF, the next step would be to extend the study to a dimer which is the minimal system where the process might occur. For dimer arrangements within the crystal structure of a chromophore, we can calculate effective electronic couplings which are indicative of the rate constant of the SF process. Nevertheless, there could be cases in which the molecular dispositions in experimentally determined crystal structures might not be the optimal arrangements where SF is enhanced. Therefore, finding dimer geometries where the electronic coupling, and hence the SF rate constant is maximised could guide the crystal engineering to obtain better molecular packings where SF is enhanced.

Our collaborators have used a frontier orbital approach to perform an exhaustive computational search of possible pair geometries for identifying the local maxima of the SF rate of cibalackrot, an indigo derivative. From experimental observations on the two different polymorphs of cibalackrot it has been concluded that the SF process is hindered by competing processes. Therefore, identifying pair geometries where SF is enhanced could help in the structural modification of the crystal structures to obtain better SF materials.

*Based on the frontier orbital approach, which relies on several approximations, 48 pair geometries of cibalackrot where the SF rate is maximised are proposed. The scope of this chapter is to compare and validate the electronic couplings computed with the frontier orbital approach against the *ab initio* Frenkel-Davydov exciton model, a higher level of theory. Results of this comparison showed that, despite the quantitative disagreement, the methodologies have a qualitative correlation and are able to discriminate between pairs with high electronic couplings. Three pair geometries are identified as the best arrangements where SF might be enhanced. The findings of this chapter suggest that the frontier orbital approach can be used for the fast and exhaustive screening of pair geometries that can be later validated with an *ab initio* methodology.*

3.1. INTRODUCTION

In the previous chapter, we presented a protocol to be followed when looking for new singlet fission (SF) materials.[1] Such protocol starts with the calculation of excitation energies for different electronic states of a single molecule. A molecule might undergo SF if they fulfil the critical energetic requirements in eqs. 1.1 and 1.2.[2] Nevertheless, looking at molecular excited state energies is just the first step. After that, it becomes necessary to extend the study to pairs of molecules since this is the minimal system where SF can take place.

For a given system, such as a dimer, the probability for SF to occur can be related to a rate constant.[7] This constant can be approximated by means of the Fermi's golden

rule[8] as explained in Section 1.5. The expression of the rate constant (eq. 1.3) clearly shows that the SF probability depends on the electronic coupling[9] (V) and on the density of states. Therefore, calculating V is an essential step to estimate SF rate constants for pair arrangements identified in the crystal structure and, as a result, it indicates the potential of the chromophore for SF applications. Nevertheless, there might be cases in which the dimer spatial arrangements found in the crystal structure are not the optimal dispositions where V is maximised. Thus, predicting pair geometries where the effective coupling is maximised (and hence the SF rate constant) can lead to crystal engineering to improve the SF yield of the chromophores.

Cibalackrot, an indigo derivative whose chemical structure is depicted in Figure 3.1, has been recently studied as a SF material.[10] Sublimation of cibalackrot leads to the formation of two different polymorphs identified as α and β . [11] These polymorphs crystallize in a monoclinic crystal system with the $P2_1/n$ and $P2_1/c$ space groups for α and β , respectively. Experimental measurements have concluded that the formation of excimers and charge-transfer species upon excitation of cibalackrot outcompete single-step SF[11] acting as traps hindering the process. Additionally, it is difficult to evaluate if the 1TT state is formed from a charge transfer (CT) state (as in SF) or by an inter-system crossing.[11]

A frontier orbital approach[2] has been developed and used to determine pair geometries of chromophores where the SF rate is maximised.[11] This model has been implemented in a computer program named "Simple". In this program, the Fermi's golden rule (within the diabatic framework and pairwise approximation) is applied. It identifies all local maxima of the rate of conversion from the S_0S_1 to the 1TT state in a molecular pair as a function of the six degrees of freedom available for the description of the mutual disposition of two rigid bodies.[11] The 48 best pair geometries (depicted in Figures 3.3, 3.4 and 3.5) where the coupling is maximised as identified by the Simple program, were chosen from our collaborators. The primary purpose of the Simple program is not the evaluation of absolute or even relative rates of SF as a function of pair geometry but the identification and approximate ranking of those geometries that are likely to be particularly advantageous for SE.[11]

The scope of this chapter is to compare the V computed with the Simple program and the V obtained with the *ab initio* Frenkel-Davydov exciton model[12, 13] (AIFDEM) for the chosen 48 pair geometries. This is done in order to verify the reliability of the approximations used for the calculation of couplings in the Simple program. The *ab initio* calculations are quite laborious, and for molecules as large as cibalackrot, such comparisons can only be made at a relatively small number of pair geometries.

The outline of this chapter is as follows: in section 3.2 we elaborate on the methodology employed for the calculation of the V using the AIFDEM. Comparison of the V calculated for the 48 pair geometries with the Simple and AIFDEM approaches is discussed in section 3.3. The concluding remarks and the outlook are given in section 3.4.

3.2. METHODOLOGY

For each dimer pair arrangement, wave functions describing particular electronic states of each constituting molecule are generated; (un)restricted Hartree-Fock wave functions are used for the description of the molecular ground state ($|\Psi_{S_0}\rangle$), cationic ($|\Psi_{D_0^+}\rangle$) and anionic ($|\Psi_{D_0^-}\rangle$) forms, whereas the singlet excited states ($|\Psi_{S_1}\rangle$) are described by configuration interaction singles (CIS) wave functions. The cc-pVDZ basis set was used. Then, spin-adapted many electron basis functions (MEBFs, $|\Xi\rangle$) describing the electronic states of the pair are constructed as spin-adapted combinations of antisymmetrized products of the molecular wave functions. Six different spin-singlet MEBFs are generated: $|\Xi_{S_0S_0}\rangle$, $|\Xi_{S_0S_1}\rangle$, $|\Xi_{S_1S_0}\rangle$, $|\Xi_{T_1T_1}\rangle$, $|\Xi_{D_0^+D_0^-}\rangle$ and $|\Xi_{D_0^-D_0^+}\rangle$. This set of MEBFs is also known as "exciton-site basis". Hamiltonian and overlap matrix elements between the MEBFs are computed, and the energies ϵ_μ and coefficients C_μ of the different μ states are determined by solving the eigenvalue problem $\mathbf{H}\mathbf{C}_\mu = \epsilon_\mu\mathbf{S}\mathbf{C}_\mu$.

The resulting state energies ϵ_μ were corrected to reference values, as stated in the original protocol[12, 13], calculated for an optimized cibalackrot molecule using time-dependent density functional theory[14] (TD-DFT) and constrained DFT[15] (c-DFT) at the ω B97X-D/cc-pVDZ level of theory. The ω B97X-D[3] functional was chosen since it gives the best description of excited state properties when compared to high-level wave function methods according to a benchmarking study performed between several popular functionals.[4–6] The $\epsilon_{S_0S_1}$ and $\epsilon_{S_1S_0}$ energies were shifted to match the vertical S_1 excitation energy ($E(S_1) = 2.94$ eV), whereas ϵ_{1TT} was shifted to twice the vertical T_1

excitation energy ($E(T_1) = 1.56$ eV) of the molecule. The reference charge transfer energies ($\epsilon_{CT} = \epsilon_{D_0^+ D_0^-}$ and $\epsilon_{D_0^- D_0^+}$) were calculated using c-DFT at the ω B97X-D/cc-pVDZ level of theory. To assess the validity of this approximation, the $\epsilon_{D_0^+ D_0^-}$ and $\epsilon_{D_0^- D_0^+}$ obtained with c-DFT were also compared with those calculated as the interaction of oxidized and reduced chromophores:

$$\epsilon_{CT} = IP - EA + C \quad (3.1)$$

where IP and EA denote the ionization potential and electron affinity of the molecule, respectively, and C represents the Coulombic attraction between the monomers in the dimer. IP and EA were calculated at the ω B97X-D/cc-pVDZ level of theory, whereas C was determined as the sum of the electrostatic attraction between the Mulliken atomic charges in the molecules in the corresponding cationic and anionic ground states. The calculated CT energies are reported in Table 3.1. The low CT state energies (approximately around 2.0 eV for 48 configurations) obtained with AIFDEM might be attributed to the spin contamination in the cationic and anionic forms. The CT state energies were then shifted to the reference values calculated with c-DFT. Interestingly, the CT state energies approximated with eq. 3.1 give lower CT states that lie between the ground state and the first excited state. The reason is that eq. 3.1 overestimates the relaxation energy of the individual molecules and only takes into account the Coulomb interaction between the charges. All calculations mentioned above were performed with the Q-Chem 5.0[16] quantum chemistry package.

Prior to the calculation of the effective electronic couplings, diabatic S[1] and S[2] states were obtained from a 2×2 non-orthogonal configuration interaction in the basis terms of the $|\Xi_{S_0 S_1}\rangle$ and $|\Xi_{S_1 S_0}\rangle$ MEBFs. The diabatic $[^1 T T]$ state corresponds to the $|\Xi_{T_1 T_1}\rangle$ MEBF. The charge transfer $|\Xi_{D_0^+ D_0^-}\rangle$ and $|\Xi_{D_0^- D_0^+}\rangle$ MEBFs were allowed to interact with the S[1] and S[2] diabatic states, resulting in 4×4 non-orthogonal configuration interaction calculation, and with the $[^1 T T]$ state giving a 3×3 NOCI calculation to study their influence on the diabatic states. Then, the effective electronic couplings between the S[1]/S[2] states and the $[^1 T T]$ state were calculated according to the direct coupling scheme[9]:

$$V_{ij} = \frac{H_{ij} - H^{av} S_{ij}}{1 - S_{ij}^2} \quad (3.2)$$

where

$$H_{ij} = \langle \Xi(S[1, 2]) | H | \Xi(^1 T T) \rangle, S_{ij} = \langle \Xi(S[1, 2]) | \Xi(^1 T T) \rangle \quad (3.3)$$

and

$$H^{av} = \frac{\langle \Xi(S[1, 2]) | H | \Xi(S[1, 2]) \rangle + \langle \Xi(^1 T T) | H | \Xi(^1 T T) \rangle}{2}. \quad (3.4)$$

Please note that this expression is identical to the one in eq. 1.4.

3.3. RESULTS AND DISCUSSION

3

Effective V were calculated with the AIFDEM methodology, as explained in Section 3.2, for the 48 configurations identified by the frontier orbitals approach. In the upcoming discussion when needed, a subscript will be added to V in order to differentiate between the methodologies with which the electronic couplings were calculated; V_{Simple} and V_{AIFDEM} . For each of the pair arrangements, two electronic coupling values are reported, $V(A)$ and $V(B)$ where A and B represent which is the photo excited molecule in the corresponding pair. Electronic couplings calculated with the Simple and AIFDEM approaches are reported in Tables 3.2 and 3.3, respectively.

Based on the absolute values of $V(A)_{Simple}$ (Table 3.2), conformation **1** shows the highest electronic coupling (41 meV) value and this suggests to be as the most efficient pair arrangement for SF. Conformation **1** corresponds to a slip-stacked like arrangement. Conformations **2** and **3** are expected to be also efficient pair orientations for SF due to their values of $V(A)_{Simple}$ which are around 33 meV. Most of the electronic couplings calculated with the Simple approach for the remaining 45 structures are within a range of 10 to 16 meV. The $V(A)_{AIFDEM}$ values (Table 3.3) also suggest conformations **1** (30 meV), **2** (23 meV) and **3** (21 meV) as the most efficient monomer dispositions for SF, although the values are lower than those calculated with the Simple approach. For the remaining configurations, the $V(A)_{AIFDEM}$ values lie between the range of 6 to 20 meV approximately. For the case in which molecule B is photo excited, the $V(B)_{Simple}$ absolute values show that conformation **1** has the highest electronic coupling, but unlike $V(A)_{Simple}$ the remaining electronic values lay in a broader range going from zero to 22 meV. For the case of $V(B)_{AIFDEM}$, high electronic couplings are observed for the first five conformations, and for the remaining ones the values lie also between a broad range between zero and 16 meV.

The correlation between the two approaches has been studied using the sum of the squares (V^2) of the electronic couplings calculated for both photo excited molecules in a pair, expressed as

$$V^2 = V(A)^2 + V(B)^2. \quad (3.5)$$

Explicit values of the V^2 for both approaches are collected in Table 3.4. The results of the correlation study are shown in Figure 3.2. Both methods seem to be able to discriminate between the structures with the highest electronic couplings (four points on the right side of Figure 3.2) and those with lower V^2 values. However, there is a weak correlation for small values of V^2 . This can be seen in the left-bottom part of Figure 3.2 in which most of the data is concentrated. This concentration of data shows that the electronic couplings of those specific configurations are within the same range (from 10 to 15 meV). The data also indicate that the AIFDEM tends to give smaller V values when compared to those obtained with the Simple approach, but a qualitative trend is observed.

Figure 3.2 | The correlation of V^2 between the Simple and AIFDEM approaches. Coefficient of determination is $R^2 = 0.70$.

3.4. CONCLUSIONS AND OUTLOOK

In this chapter, we compared the electronic couplings calculated with a frontier orbital (also referred to as Simple) approach against the ones calculated with AIFDEM for 48 pair geometries. These pairs of molecules are predicted to be optimal spatial dispositions where the SF rate is maximised. Based on the electronic couplings calculated with both approaches, conformation **1** is predicted to be the most efficient pair for SF to occur. Interestingly, this pair corresponds to a slip-stacked arrangement. The couplings also reveal that conformations **2** and **3** are also expected to be efficient for the conversion to the 1TT state. The remaining 45 structures have similar electronic couplings and could not be discriminated among them.

The V_{AIFDEM} values are lower than those calculated with the frontier orbital (or Simple) approach. A correlation between both approaches has been discussed. Both approaches show a satisfactory qualitative behaviour and it suggests that the results of the Simple procedure are meaningful. We concluded that the methods are able to discriminate clearly between those pair geometries with larger V (e.g. conformations **1**, **2** and **3**) from those that exhibit lower V values. Conformation **1**, from the ones explored in this chapter, is expected to be the most efficient disposition for SF.

The results of this chapter suggest that the Simple procedure can be used as a first step for the exhaustive screening of pair geometries where SF might be enhanced. Then, a higher level of theory can be used for further investigation and validation of those dimers. Based on this information, structural modifications in the crystal structures of the potential SF chromophores can be attempted in order to obtain better molecular packing where the SF process is enhanced. This chapter has discussed electronic couplings as a

fundamental quantity to study SE, However, we can look at the SF process from another point of view employing an excited state analysis which is the scope of the following chapters.

3.5. APPENDIX

3.5.1. DEPICTION OF THE FORTY EIGHT PAIR GEOMETRIES

Figure 3.3 | Depiction of the first sixteen of 48 pair arrangements exhibiting the highest electronic coupling calculated with the frontier orbitals method.

Figure 3.4 | Depiction of the second sixteen of 48 pair arrangements exhibiting the highest electronic coupling calculated with the frontier orbitals method.

Figure 3.5 | Depiction of the third sixteen of 48 arrangements exhibiting the highest electronic coupling calculated with the frontier orbitals method.

3.5.2. CHARGE TRANSFER STATE ENERGIES OF THE PAIR GEOMETRIES

Table 3.1 | Charge transfer state energies (in eV) of the forty-eight pair geometries using an interaction of oxidized and reduced chromophores approximation (O/R) and constrained DFT (c-DFT).

Config.	E(CT) (O/R)	E(CT) (c-DFT)	Config.	E(CT) (O/R)	E(CT) (c-DFT)
1	2.63	3.71	25	2.81	3.98
2	2.94	3.85	26	2.81	4.32
3	2.74	4.04	27	2.83	3.77
4	2.85	3.81	28	3.20	3.70
5	2.70	3.94	29	2.74	4.32
6	2.52	4.11	30	2.74	4.16
7	2.91	4.07	31	2.49	4.51
8	2.70	3.93	32	2.70	4.26
9	2.69	4.02	33	2.44	3.73
10	2.52	4.08	34	2.93	4.33
11	2.89	4.28	35	3.17	3.83
12	2.91	4.22	36	2.79	4.46
13	2.73	4.09	37	2.81	3.98
14	2.52	4.45	38	2.69	4.02
15	3.30	3.40	39	2.71	4.22
16	2.67	4.01	40	2.69	4.03
17	2.59	4.11	41	3.14	3.61
18	2.75	3.82	42	2.74	4.03
19	2.91	4.22	43	2.80	3.98
20	2.90	3.82	44	2.71	4.30
21	2.89	3.75	45	2.74	4.33
22	2.90	4.18	46	2.67	4.10
23	2.55	4.07	47	2.31	4.91
24	2.84	4.01	48	2.90	3.91

3.5.3. ELECTRONIC COUPLINGS OF THE CONFIGURATIONS CALCULATED WITH THE SIMPLE APPROACH

Table 3.2 | Absolute values of the electronic couplings (in meV) of the forty-eight pair geometries calculated with frontier orbital approach (Simple program) for the two different $S_0 S_1$ (V(A)) and $S_1 S_0$ (V(B)).

Configuration	V(A)	V(B)	Configuration	V(A)	V(B)
1	41.2	41.5	25	15.2	10.0
2	32.6	8.9	26	14.9	22.2
3	33.3	14.8	27	14.3	14.3
4	16.4	21.9	28	11.1	3.5
5	24.9	19.7	29	13.5	4.8
6	15.6	10.6	30	12.5	13.2
7	17.7	7.5	31	12.9	1.9
8	20.9	16.4	32	12.3	8.2
9	14.9	10.9	33	11.8	11.5
10	13.4	1.1	34	12.9	11.8
11	14.3	2.0	35	8.4	7.7
12	16.4	0.6	36	16.7	2.5
13	13.4	13.4	37	14.1	6.9
14	14.7	5.2	38	14.2	6.9
15	16.7	5.5	39	12.7	9.3
16	14.9	7.9	40	14.7	11.0
17	13.5	4.9	41	20.2	12.1
18	11.6	5.1	42	10.6	4.7
19	16.3	0.6	43	15.3	10.0
20	11.9	13.9	44	11.1	1.4
21	12.9	13.2	45	13.4	4.6
22	10.9	1.3	46	10.9	8.9
23	15.2	2.6	47	12.9	1.0
24	9.7	5.5	48	10.8	8.7

3.5.4. ELECTRONIC COUPLINGS OF THE CONFIGURATIONS CALCULATED
WITH AIFDEM

Table 3.3 | Electronic couplings (in meV) of the forty-eight pair geometries calculated with AIFDEM for the two different S_0S_1 (V(A)) and S_1S_0 (V(B)).

Configuration	V(A)	V(B)	Configuration	V(A)	V(B)
1	30	10.5	25	13.7	5.7
2	22.8	9	26	5.9	16.6
3	21.0	12.9	27	13.1	2.6
4	21.4	18.2	28	10	3.2
5	24.8	16.6	29	14.9	4.7
6	14.2	11.9	30	13.7	5.6
7	20	8.5	31	12.1	2.1
8	21.2	16.2	32	15.5	6.6
9	15.7	13	33	12.5	10.9
10	15.4	2.5	34	13.3	13.7
11	15.3	0.5	35	9.7	8.7
12	12.7	9.5	36	12.7	1.4
13	13.1	11.4	37	12.2	5.1
14	17.4	2.1	38	16.1	6
15	15.4	4.9	39	16.8	6.1
16	15.8	5.9	40	14.2	12.2
17	13.9	2.2	41	19.4	12.2
18	13.2	3.7	42	15.2	2.3
19	12.7	1.1	43	11.4	4.2
20	13.9	10.9	44	12.5	0.8
21	15.7	11.3	45	16.5	2.4
22	11.1	2.5	46	13.3	10.7
23	13.2	5.9	47	12.3	0.9
24	11.4	4.1	48	7.8	6.3

3.5.5. SQUARE VALUES OF THE SUM OF THE ELECTRONIC COUPLINGS FOR THE FORTY EIGHT PAIR GEOMETRIES

Table 3.4 | Square values (in meV^2) of the sum of the electronic couplings calculated for the Simple and AIFDEM approaches. V^2 is defined as $V(A)^2 + V(B)^2$.

Configuration	V_{Simple}^2	V_{AIFDEM}^2	Configuration	V_{Simple}^2	V_{AIFDEM}^2
1	3418	1010	25	332	220
2	1145	600	26	717	310
3	1330	607	27	409	178
4	748	789	28	135	110
5	1007	890	29	204	244
6	354	343	30	330	219
7	370	472	31	172	150
8	708	711	32	218	283
9	341	415	33	271	275
10	179	243	34	309	364
11	209	234	35	130	169
12	269	251	36	284	163
13	359	301	37	248	174
14	244	307	38	249	295
15	307	261	39	246	319
16	283	284	40	336	225
17	207	198	41	554	377
18	160	187	42	135	236
19	266	162	43	335	147
20	339	312	44	126	156
21	341	374	45	201	278
22	120	129	46	200	291
23	237	209	47	166	152
24	124	146	48	191	100

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4

AN EXCITED STATE ANALYSIS ON TETRACENE: APPLICATION ON SINGLET FISSION

ABSTRACT

4

In the previous chapters we have presented and discussed a protocol for (1) the finding of new singlet fission molecules based on energetic criteria, and (2) the calculation of electronic couplings which are related to the probability of singlet fission to occur in a system. In this chapter, we explore singlet fission from another point of view by employing an excited state analysis to identify and characterize the excited states of a chromophore and their direct relation with the singlet fission process.

We study the excited states of three pairs of tetracene with different relative orientation in the crystal structure showing different electronic couplings and identify the role of charge transfer states. First, a suitable theoretical method for the study of the tetracene pairs is determined by comparing time-dependent density functional theory with wave function-based methods in terms of excitation energies, so-called exciton descriptors, and graphical tools such as electron-hole correlation plots and natural transition orbitals.

The results show the presence of low-lying charge transfer states in those tetracene pairs with non-zero electronic coupling, suggesting a superexchange-mediated mechanism, and high-lying charge resonance states for the pair with zero electronic coupling. Finally, the lower electron-hole correlation coefficients for pairs with non-zero coupling speak in favor of the superexchange-mediated mechanism, as a weaker Coulombic attraction due to the mixing with charge transfer states further facilitates the formation of the 1TT state from the photoexcited molecule. Additionally, we demonstrate the applicability of the excited state analysis to study the singlet fission process opening the door for further investigations in another potential singlet fission molecules.

4.1. INTRODUCTION

Theoretical studies have been performed in order to find new singlet fission (SF) molecules that fulfill the critical energetic criteria $E(S_1) > 2E(T_1)$, [1, 2] and also to understand its underlying mechanism (a detailed review can be found in Ref. [3]) but many questions of how this process actually occurs are still active areas of research; these include the role of the vibrational modes [4–8] and charge transfer (CT) states [9, 10] in the SF process.

Generally, the simple picture in which the two coupled triplets (1TT) are formed from the local excitations (S_0S_1 and S_1S_0) via a direct two-electron transfer is accepted (blue arrow in Fig. 4.1). However, CT states ($D_0^+D_0^-$ and $D_0^-D_0^+$) have been believed to play an essential role in the conversion to the 1TT state; if the energy of these states is close to the energy of the S_1 state a charge hopping [11] mechanism can occur, in which the CT states are populated and the process occurs involving them (green arrow in Fig. 4.1), but if the CT state energies are higher than S_1 , then a CT-mediated superexchange [11] process might occur where CT states mix with the initial and final states facilitating the

conversion (red arrow in Fig. 4.1). Thus, it is crucial to determine the energetic location of CT states to identify the underlying mechanism of the SF process.

Figure 4.1 | Singlet fission process occurring via three different mechanisms: a molecule is excited upon absorption of a photon, then the excited molecule transfers part of its energy to a neighbour to form two triplets. S_0 = ground state, S_1 = lowest singlet, T = triplet, D_0^+ = cation and D_0^- = anion.

The identification, characterisation and investigation of the excited states of a molecule and their relation with the SF process can be aided by quantum chemical calculations. Recently a series of excited state analysis tools (also known as exciton descriptors) based on the one-electron transition density matrix (1TDM) and its molecular orbital representation have been developed.[12, 13] In this work a subset of exciton descriptors based on the 1TDM as well as graphic tools such as electron-hole correlation plots and natural transition orbitals, were used to analyze the excited states of tetracene, a widely known molecule that experimentally exhibits SF[6, 7, 9, 14–18], in its monomeric, dimeric and trimeric forms. Our results provide detailed insights into the role of the CT states in the SF process for the pairs of tetracene molecules.

The chapter is organized as follows: a subset of the exciton descriptors and how they can be applied to identify the character of an excited state are described in section 4.2.1. In section 4.2.2 calculation of electronic couplings, which are proportional to the rate of the SF process, is discussed using a nonorthogonal configuration interaction approach. Then, in section 4.4.1 we compare the performance of linear response time-dependent density functional theory[19] (TD-DFT) against wave function-based methods using a tetracene molecule in order to determine a suitable functional for the description of the tetracene pairs. In section 4.4.2 the excited states of three tetracene pairs with different relative

orientation and electronic couplings are characterised based on the exciton descriptors and the role of the CT and charge resonance states in the SF process is analyzed. Our concluding remarks are given in section 4.5.

4.2. THEORY

4.2.1. EXCITON ANALYSIS AND EXCITON DESCRIPTORS

The central property in the excited state analysis is the 1TDM between the ground (Ψ_0) and excited (Ψ_I) state.[12] The 1TDM offers a compact description of an electronic transition, i.e. it describes concisely the electron-hole pair formed upon absorption of a photon.[20] The matrix representation in an orbital basis set $\{\chi_\eta\}$ of the 1TDM takes the form[21]

$$\gamma^{0I}(r_h, r_e) = \sum_{\mu\nu} D_{\mu\nu}^{0I} \chi_\mu(r_h) \chi_\nu(r_e) \quad (4.1)$$

where $\chi_\mu(r_h)$ and $\chi_\nu(r_e)$ represent the μ and ν orbitals where the positively-charged electron-hole and the negatively-charged excited electron are located, respectively. The 1TDM element $D_{\mu\nu}^{0I}$ is defined as $D_{\mu\nu}^{0I} = \langle \Psi_0 | \hat{a}_\mu^\dagger \hat{a}_\nu | \Psi^I \rangle$, where $\hat{a}_\mu^\dagger$ and $\hat{a}_\nu$ are the one-particle creation and annihilation operators, respectively. γ^{0I} can be then used to compute the so-called exciton descriptors that allow to identify, characterise and investigate the nature of the excited states of a molecule. The details of how the descriptors are computed from the 1TDM are beyond the scope of this work but the reader is referred to Ref. [12] for further details. In the following, a short overview of a subset of the exciton descriptors and how to apply them in an excited state analysis is provided. The characterisation of the excited states based on the above mentioned tools has been discussed in more details previously,[22] and for a more detailed discussion on the theory behind this excited state analysis the interested reader is referred to Ref. [12, 13, 20].

One of the analysis that can be done on the 1TDM is to partially integrate its square while restricting the hole to a fragment A and the electron to a fragment B , [23] represented as

$$\Omega_{AB} = \int_A \int_B \gamma^{0I}(r_h, r_e)^2 dr_e dr_h. \quad (4.2)$$

Ω_{AB} are the so-called charge-transfer numbers and represent the probability of finding the hole on fragment A while the electron is on fragment B , [12] or in practical terms indicate from where to where the electron density is transferred during the excitation (which could be pairs or group of atoms). A useful way to analyze Ω_{AB} , particularly when more than two fragments are defined, are the so-called electron-hole correlation plots. These plots are generated by partitioning the system into fragments and computing the Ω_{AB} between them; the resulting values are visualized as a pseudo-color matrix with size $n \times n$ where n is the number of fragments.[23] Local excitations correspond to the diagonal of the matrix going from lower left to upper right,[24] whereas CT contributions occurring between the fragments are indicated in the off-diagonal elements. Additionally to the visualization of Ω_{AB} , the off-diagonal contributions can be summed up to obtained the so-called total charge transfer (ω_{CT}) number defined as[25]

$$\omega_{CT} = \frac{1}{\Omega} \sum_{A, B \neq A} \Omega_{AB}, \quad (4.3)$$

with Ω being the squared (Frobenius) norm

$$\Omega = \langle \gamma^{0I} | \gamma^{0I} \rangle. \quad (4.4)$$

Ω indicates the single excitation character of an excited state and its value is typically in the range between zero and one, where one indicates a pure single excited state.[23] For TDA-TDDFT, used in this paper, the value of Ω is always one, by definition. [26] The values of ω_{CT} go from zero to one, in which zero corresponds to a local excitation and one to a completely separated CT state.[21] This descriptor is useful to preliminarily determine if an excited state corresponds to a local excitation or a CT state, however such assignment shall be done analyzing more than one exciton descriptor as it will be discussed later.

As stated above, the first step is to determine the character of a particular excited state, i.e., if it corresponds to a local excitation, to a Rydberg state or a CT state. The identification of CT states is rather challenging from the theoretical point of view, and it is important to differentiate between two types: (1) CT states in which there is a permanent shift of the electron density, and (2) charge-resonance (CR) states in which no net charge transfer occurs.[22] The identification of these states could be confusing, but CT and CR states can be distinguished by measuring the distance between the centroids of the electron and hole expressed as[22]

$$d_{h \rightarrow e} = |\langle \vec{x}_e - \vec{x}_h \rangle_{exc}|, \quad (4.5)$$

where $\vec{x}_e$ and $\vec{x}_h$ are the positions of the centroids of the electron and hole, respectively. If for an excited state $d_{h \rightarrow e} > 0$ this can be identified as a CT state, whereas $d_{h \rightarrow e} = 0$ might indicate either a CR state or a local excitation. In order to confirm if the state corresponds to a CR or a local excitation, the so-called exciton size (d_{exc}) can be used which measures the root-mean-square separation distance between the hole and the electron taking into consideration their spatial distributions.[22] d_{exc} is defined as

$$d_{exc} = \sqrt{\langle |\vec{x}_h - \vec{x}_e|^2 \rangle_{exc}}. \quad (4.6)$$

Their values are rather different for local excitations and CR states as described later. Such difference can only be seen when comparing the corresponding d_{exc} values of the excited states for a specific system.

The next two descriptors described in this work correspond to the electron and hole sizes denoted as σ_e and σ_h , respectively, and expressed as[22]

$$\sigma_h = \sqrt{\langle \vec{x}_h^2 \rangle_{exc} - \langle \vec{x}_h \rangle_{exc}^2} \quad (4.7)$$

and

$$\sigma_e = \sqrt{\langle \vec{x}_e^2 \rangle_{exc} - \langle \vec{x}_e \rangle_{exc}^2}. \quad (4.8)$$

These quantities represent the spatial distribution of the hole and the electron with respect to their centroids. σ_e and σ_h are useful to differentiate between types of excited states where σ_e and σ_h are rather different, e.g. Rydberg states, core-excitations, etc., with σ_e the key quantity to differentiate Rydberg from valence states.[20] The last descriptor

presented in this work is the so-called electron-hole correlation coefficient (R_{eh}) defined as

$$R_{eh} = \frac{COV(r_h, r_e)}{\sigma_h \sigma_e} \quad (4.9)$$

where $COV(r_h, r_e) = \langle \vec{x}_h \cdot \vec{x}_e \rangle_{exc} - \langle \vec{x}_h \rangle_{exc} \cdot \langle \vec{x}_e \rangle_{exc}$, which describes the spatial relation between the electron and hole. Its values go from -1 to +1, and the sign of R_{eh} gives information about the joint exciton; negative values indicate that the electron and hole avoid each other in space. On the opposite, positive values suggest that the exciton is bound by electrostatic interaction, and if $R_{eh} = 0$ there is no electron-hole correlation.[27]

Another useful graphic tool in the description of an excited state are the so-called natural transition orbitals (NTOs). The NTOs result from a single-value decomposition of the 1TDM and give a compact and state-specific description of the excitation.[12] With having all these tools in hand, one can go beyond the classical approach of visualizing orbitals by analyzing the exciton descriptors described above.

4

4.2.2. ELECTRONIC COUPLINGS

The probability of SF to occur in a system can be approximated by means of the Fermi's golden rule:[28]

$$k_E \approx \frac{2\pi}{\hbar} |V_{if}|^2 \rho(E) \quad (4.10)$$

where V_{if} represents the electronic coupling between two (diabatic) states, i and f , and $\rho(E)$ denotes the density of states per energy E unit. Electronic couplings have been evaluated with different approaches,[3, 29] but in this work a nonorthogonal configuration interaction (NOCI) approach is employed, which is interesting for the SF process since the interaction between the states can be calculated directly.[2, 30]

In the NOCI approach, wave functions for the monomers in a cluster of N molecules describing the S_0 , S_1 , T_1 , D_0^+ and D_0^- states are generated. These molecular wave functions can be chosen to be of the CASSCF-type. In this work, the study is restricted to pairs of molecules. Then, many-electron basis functions (MEBFs) representing the following electronic states of the pair of molecules are generated as antisymmetrized products of the molecular wave functions: $|\Phi_{S_0 S_0}\rangle$, $|\Phi_{S_0 S_1}\rangle$, $|\Phi_{S_1 S_0}\rangle$, $|\Phi_{1 TT}\rangle$, $|\Phi_{D_0^+ D_0^-}\rangle$ and $|\Phi_{D_0^- D_0^+}\rangle$. Hamiltonian and overlap matrix elements between the MEBFs are calculated, and the electronic coupling is obtained according to[31]

$$V_{if} = \frac{\langle \Phi_i | \hat{H} | \Phi_f \rangle - \frac{\langle \Phi_i | \hat{H} | \Phi_i \rangle + \langle \Phi_f | \hat{H} | \Phi_f \rangle}{2} \cdot \langle \Phi_i | \Phi_f \rangle}{1 - \langle \Phi_i | \Phi_f \rangle^2} \quad (4.11)$$

where i and f are the initial and final states of interest, respectively, which in the case of SF correspond to the photoexcited monomers ($|\Phi_{S_0 S_1}\rangle$ and $|\Phi_{S_1 S_0}\rangle$) and the singlet-coupled triplet state ($|\Phi_{1 TT}\rangle$).

4.3. COMPUTATIONAL DETAILS

Ground state optimisation was carried out at the ω B97X-D/ANO-S-VDZP level of theory, including Grimme's dispersion correction.[32] Excited state calculations were carried out using TD-DFT within the Tamm–Dancoff approximation with a variety of functionals: BLYP, B3LYP, BHLYP, CAM-B3LYP and ω B97X-D. Additionally, two variants of the algebraic diagrammatic construction of second order[33] (ADC(2)-s and ADC(2)-x) and equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) were used. The methods were employed with the 6-31G, 6-311G, cc-pVDZ, cc-pVTZ and ANO-S-VDZP basis sets. All calculations mentioned above were performed with the Q-Chem 5.1 quantum chemistry package.[34] Pairs of tetracene molecules were identified and taken from the optimised crystal structure (see Section 4.6.1 for crystal structure optimization). Excited state analysis was performed on the pairs of tetracene at the TD-DFT/ANO-S-VDZP level of theory employing CAM-B3LYP and ω B97X-D.

Fig. 4.2 shows the symmetric fragmentation of tetracene used in this work; three different fragments resulted with two benzene-like rings in the outer and a six-carbon fragment in the middle. Based on this fragmentation, the electron-hole correlation plots for the four lowest singlet excited states of the pairs are obtained at the CAM-B3LYP/ANO-S-VDZP and ADC(2)-s/ANO-S-VDZP levels of theory. Post-processing of results and electron-hole correlation plots were generated with the TheoDORÉ 1.7.2 analysis package.[24, 35] In this work we use a grey scale for the electron-hole correlation plots with black corresponding to the highest Ω_{AB} and white to zero (or lowest Ω_{AB}).

Figure 4.2 | Labelled fragmentation scheme of the tetracene molecule used for the calculation of Ω_{AB} and construction of the electron-hole correlation plots.

For the electronic coupling calculations, the molecular wave functions for the pairs of tetracene molecules were generated at the CASSCF(4,4)/cc-pVDZ level of theory using the GAMESS-UK package.[36] Then, the protocol outlined in Ref. 2 was employed to obtain the diabatic states. The GronOR package [30] was used to compute the Hamiltonian and overlap matrix elements between the states. Electronic couplings were calculated as defined in section 4.2.2, allowing the mixing of the MEBFs describing the CT states to the S_1 and 1TT states.

4.4. RESULTS AND DISCUSSION

4.4.1. TETRACENE MOLECULE

Table 4.1 collects the excitation energies and oscillator strengths (f) for the four lowest singlet excited states of the tetracene molecule calculated with TD-DFT (various functionals) as well as wave function based methods using ANO-S-VDZP basis set. In a previous tetracene study [37], the ANO-S-VDZP basis set was found to have a superior performance than other polarised double- ζ basis sets in the excitation energies, wave function overlaps and matrix-based descriptors. Influence of the basis set on excitation energies and state order was also investigated in this work; despite the differences in excitation energies, the state orders remain the same for all the methods independently of the basis set used (see Tables 4.6, 4.7, 4.8 and 4.9). ADC(s)-x is not included in this discussion since it gives an overall unbalanced description of the excited states and an underestimation of the excitation energies (see Tables 4.6, 4.7, 4.8 and 4.9).[33] One observes the typical blueshift of all four lowest states to higher excitation energies when the fraction of Hartree-Fock (HF) exchange is increased from zero (BLYP) to 20% (B3LYP), and finally to 50% (BHLYP). The state order remains the same for the functionals with HF fraction higher than zero and it is similar to the state order in ADC(2)-s and EOM-CCSD (see Table 4.1). These results suggest that tetracene can be satisfactorily described by TD-DFT because of its closed-shell configuration, being also a planar molecule not prone to intramolecular charge transfer. In addition, increasing the size of the basis set by adding more diffuse basis functions has negligible effect on excitation energy and state order, suggesting these states being local excited states.[20]

Table 4.1 | Excitation energies (in eV) and oscillator strengths (in parentheses) for the four lowest singlet excited states of a tetracene molecule calculated at different levels of theory with ANO-S-VDZP as basis set. ^aReference [38]: experimental value of the gas-phase vertical excitation energy. ^bReference [39]: measurement on the crystal. ^cReference [37]: also used ANO-S-VDZP as basis set.

Method	S_1	S_2	S_3	S_4
BLYP	2.36(0.057)	3.00(0.000)	3.22(0.002)	3.77(0.000)
B3LYP	2.64(0.087)	3.48(0.003)	3.60(0.000)	4.12(0.000)
BHLYP	3.02(0.137)	3.72(0.003)	4.41(0.000)	4.59(0.000)
ω B97X-D	3.07(0.141)	3.74(0.004)	4.49(0.000)	4.68(0.000)
CAM-B3LYP	3.01(0.133)	3.71(0.004)	4.41(0.000)	4.55(0.000)
ADC(2)-s	2.92(0.096)	3.57(0.002)	4.31(0.000)	4.49(0.000)
EOM-CCSD	3.00(0.104)	3.56(0.003)	4.72(0.000)	4.89(0.000)
exp.	2.88 ^a			
exp. (crystal)	2.39 ^b			
CASPT2(12,12)	2.87 ^c			

From Table 4.1, ADC(2)-s/ANO-S-VDZP and EOM-CCSD/ANO-S-VDZP, have a very close agreement to the gas-phase experimental value for S_1 by 0.04 and 0.12 eV, respectively. However, also for S_1 the excitation energy is overestimated by 0.53 eV (ADC(2)-s)

and 0.61 eV (EOM-CCSD) when compared against the value measured in the crystal structure of 2.39 eV[39] and this can be attributed to the fact that no environmental effects were considered in our calculations. The S_1 excitation energies calculated with ADC(2)-s and EOM-CCSD are also in line with a previously reported excitation energy calculated at the CASPT2/ANO-S-VDZP level of theory (2.87 eV[37]) by about 0.05 and 0.13 eV, respectively. In the case of the remaining states where to the best of our knowledge no experimental values are available, ADC(2)-s and EOM-CCSD have a close agreement for S_2 (0.01 eV of difference) but they deviate for the higher S_3 and S_4 states where the differences are approximately 0.4 eV. In the following, the method selection is restricted to the spectroscopically relevant states S_1 and S_2 (usually termed as 1L_a and 1L_b), whereas S_3 and S_4 will be kept and discussed to show the applicability of the exciton descriptors.

Comparing the performance of TD-DFT and ADC(2)-s wave function-based methods, i.e. ADC(2)-s and EOM-CCSD in Table 4.1, it is apparent that functionals containing a larger amount of HF exchange (>50%), i.e. B3LYP, ω B97X-D, and CAM-B3LYP, perform in a close agreement (difference of ≈ 0.1 eV) with ADC(2)-s and EOM-CCSD. A similar trend is observed for S_2 , with slightly higher deviation (difference of ≈ 0.15 eV).

Earlier studies on tetracene[40, 41] and other large π -conjugated systems[20, 22] have revealed that CAM-B3LYP is a suitable functional when describing excitation energies[40] and exciton descriptors.[20, 22, 41] Following these conclusions, the exciton descriptors (Ω , d_{exc} , $d_{h \rightarrow e}$, σ_h , σ_e and R_{eh}) for the four lowest singlet excited states were then calculated with the long-range corrected functionals ω B97X-D and CAM-B3LYP and compared with the wave function-based methods, i.e. ADC(2)-s and EOM-CCSD; Table 4.2 collects these results.

The difference in Ω values between TD-DFT and ADC(2)-s and EOM-CCSD in Table 4.2 comes from the fact that TD-DFT (within the adiabatic approximation) does not consider double and/or higher excitations, and therefore the transitions are predicted as pure single excitation character for all functionals. In contrast, values lower than one obtained with ADC(2)-s ($\Omega \approx 0.81$) and EOM-CCSD ($\Omega \approx 0.75$) can be attributed either to orbital relaxation effects or to a partial double excitation character of the state. For our purpose, these effects are not explored but a further discussion on how to identify and study them can be found in Ref. [13].

The values of $d_{h \rightarrow e}$ which are zero for all states independently of the method of choice, indicate that these states do not have pronounce CT character and can be safely labeled as local excitations. However, ω_{CT} values (≈ 0.60) calculated for both TD-DFT and the wave function-based methods suggest that these states are not pure local excitations and contain some CT character. This will be further discussed in relation to the corresponding electron-hole correlation plots presented later in this section. It is worth to point out that both Ω_{AB} and ω_{CT} depend on the fragmentation scheme used. ω_{CT} values in Table 4.2 are calculated with the fragmentation scheme in Fig. 4.2. Calculating ω_{CT} and creation of electron-hole correlation plots for EOM-CCSD is not currently supported in TheoDOR.

An overall inspection of the d_{exc} , σ_h , σ_e and R_{eh} descriptors, in Table 4.2 reveals that the calculated values for the states of interest in this work, i.e. S_1 and S_2 , are very similar for all employed levels of theory. For the higher lying states S_3 and S_4 states, slight deviations can be observed. If one focuses on d_{exc} values at ADC(2)-s and EOM-CCSD level of theories for S_3 and S_4 , it becomes evident that they show a different state order. A

Table 4.2 | Exciton descriptors of the four lowest singlet excited states of the tetracene molecule calculated at different levels of theory with ANO-S-VDZP as basis set. NA = Not available. EOM-CCSD currently not supported in TheoDOR for ω_{CT}

Method	State	Ω	d_{h-e} (Å)	d_{exc} (Å)	ω_{CT}	σ_h (Å)	σ_e (Å)	R_{eh}
ω B97X-D	S_1	1	0	4.525	0.60	3.255	3.332	0.056
	S_2	1	0	4.107	0.60	3.201	3.293	0.200
	S_3	1	0	4.059	0.61	3.736	3.353	0.348
	S_4	1	0	5.051	0.67	3.061	3.629	-0.134
CAM-B3LYP	S_1	1	0	4.629	0.61	3.288	3.367	0.032
	S_2	1	0	4.188	0.61	3.224	3.316	0.180
	S_3	1	0	4.784	0.65	3.736	3.166	0.047
	S_4	1	0	4.601	0.65	3.126	3.857	0.144
ADC(2)-s	1^1B_{2u}	0.81	0	4.553	0.59	3.284	3.348	0.057
	1^1B_{3u}	0.80	0	4.093	0.59	3.240	3.325	0.223
	1^1B_{1g}	0.79	0	5.028	0.66	3.640	3.178	-0.084
	2^1B_{1g}	0.81	0	4.312	0.61	3.254	3.846	0.271
EOM-CCSD	1^1B_{2u}	0.76	0	4.442	NA	3.248	3.327	0.087
	1^1B_{3u}	0.75	0	3.901	NA	3.167	3.253	0.262
	1^1B_{1g}	0.76	0	4.147	NA	3.759	3.317	0.318
	2^1B_{1g}	0.74	0	4.830	NA	3.070	3.733	0.001

possible explanation for that is the small energy gap between the two states (see Table 4.1). Therefore, the analysis and interpretation of these states is not straightforward.

Local excitation character for the S_1 and S_2 states is supported by the fact that $\sigma_e \approx \sigma_h$ (less than 0.1 Å) at all level of theories applied here; similar hole and electron sizes indicate valence states.[20] Interestingly, σ_e and σ_h calculated using ω B97X-D and CAM-B3LYP functionals are very similar to the corresponding values calculated at ADC(2)-s and EOM-CCSD level of theories. The R_{eh} magnitudes for the S_1 and S_2 states are similar between TD-DFT and the wave function-based methods, in the case of S_1 this is in the order of 10^{-2} and for S_2 between the 0.180-0.262 range. Moreover, all of them are positive values (for S_1 and S_2) which indicates an attractive correlation between the electron and the hole.

In Fig. 4.3 the electron-hole correlation plots of the tetracene molecule calculated with CAM-B3LYP and ADC(2)-s for the fragmentation scheme depicted in Fig. 4.2 are shown. For the S_1 state, the exciton is slightly delocalised over the whole system with the main contribution in the central fragment (fragment 2 in Fig. 4.2). Some CT occurs between neighbouring fragments but in a lesser extent (grey areas in the off-diagonal elements), as predicted from the ω_{CT} values in Table 4.2. In S_2 we observe that the exciton is also delocalised across the molecule as in S_1 but (1) the contribution from the central fragment is reduced, (2) the local excitation character in the extremes is enhanced, and (3) the CT between nearest neighbours is still present and slightly enhanced. The behavior changes in higher excited states, e.g. S_3 is predicted to be a local excitation with CT occurring from

the benzene rings in the extremes towards the central fragment (from fragments 1 and 3 to 2). S_4 is also a local exciton but the CT occurs from the central fragment towards the benzene rings (from fragment 2 to 1 and 3). The electron-hole correlation plots calculated with CAM-B3LYP are very similar to those obtained with ADC(2)-s (see Fig. 4.3), which suggests the Coulomb-attenuated functional as a suitable functional for studying larger systems, namely tetracene pairs presented in section 4.4.2.

Figure 4.3 | Electron-hole correlation plots calculated at the a) CAM-B3LYP/ANO-S-VDZP and b) ADC(2)-s/ANO-S-VDZP level of theory for the four lowest singlet excited states of the tetracene molecule. e and h denote the electron and hole coordinates, respectively. Numbers represent the units in the fragmentation scheme depicted in Fig. 4.2

NTO transitions, weights and character of the states are shown in Table 4.3 and the state-averaged NTOs, obtained with CAM-B3LYP, involved in the transitions are depicted in Figure 4.4. In this discussion, the NTOs corresponding to the hole are represented as h_i and the electron (or particle) as e_i with i being the corresponding i -th orbital. As discussed at the end of section 4.2.1, exciton descriptors allow us to go beyond the common approach of simply analyzing orbitals. Particularly when the orbitals of interest look very similar to each other and no precise conclusions can be drawn from them, which is the case for the NTOs of tetracene in Figure 4.4. The delocalization across the molecule is similar for the six orbitals involved in the transitions of the four lowest singlet states. Nevertheless, the character of the states can be assigned based on the NTOs. For instance, S_1 has a $\pi \rightarrow \pi^*$ character, with the transition occurring from h_1 to e_1 with a weight of 0.94, which means that 94% of the S_1 state is described by this NTO transition. S_2 is composed by two NTO transitions of almost equal weight (0.51 and 0.46) and it corresponds to an overall $\pi \rightarrow \pi^*$ character. For S_3 , the transition goes from h_3 to e_1 with

a high weight of 0.95 and it corresponds to a $\pi \rightarrow \pi^*$ character. Similar results can be seen for the S_4 state. The results for CAM-B3LYP are similar to those obtained with ADC(2)-s and EOM-CCSD (see Table 4.3). The NTOs for ADC(2)-s and EOM-CCSD are provided in Figure 4.8.

Table 4.3 | NTO transitions, weights and character of the four lowest singlet excited states of the tetracene molecule calculated at CAM-B3LYP, ADC(2)-s, and EOM-CCSD level of theories using ANO-S-VDZP as basis set.

State	Transition	CAM-B3LYP		ADC(2)-s			EOM-CCSD		
		Weight	Character	Transition	Weight	Character	Transition	Weight	Character
S_1	$h_1 \rightarrow e_1$	0.94	$\pi \rightarrow \pi^*$	$h_1 \rightarrow e_1$	0.79	$\pi \rightarrow \pi^*$	$h_1 \rightarrow e_1$	0.72	$\pi \rightarrow \pi^*$
S_2	$h_2 \rightarrow e_1$	0.51	$\pi \rightarrow \pi^*$	$h_2 \rightarrow e_1$	0.41	$\pi \rightarrow \pi^*$	$h_2 \rightarrow e_1$	0.40	$\pi \rightarrow \pi^*$
	$h_1 \rightarrow e_2$	0.46	$\pi \rightarrow \pi^*$	$h_1 \rightarrow e_2$	0.37	$\pi \rightarrow \pi^*$	$h_1 \rightarrow e_2$	0.35	$\pi \rightarrow \pi^*$
S_3	$h_3 \rightarrow e_1$	0.95	$\pi \rightarrow \pi^*$	$h_3 \rightarrow e_1$	0.73	$\pi \rightarrow \pi^*$	$h_3 \rightarrow e_1$	0.68	$\pi \rightarrow \pi^*$
S_4	$h_1 \rightarrow e_3$	0.95	$\pi \rightarrow \pi^*$	$h_1 \rightarrow e_3$	0.74	$\pi \rightarrow \pi^*$	$h_1 \rightarrow e_3$	0.73	$\pi \rightarrow \pi^*$

4

The interpretation dependency on the fragmentation scheme has been previously discussed. [23] To explore this influence, the tetracene molecule was fragmented asymmetrically in two, four and five units and the electron-hole correlation plots are shown in Figure 4.9. The plots show patterns that are difficult to interpret and relate to the NTO analysis. Previously another scheme with five fragments in tetracene was reported. [21]. Symmetric fragmentation is suggested to be the most suitable choice when possible, as it is done in this work, and if the units are not chemically equivalent the results should be analyzed with care.[21]

Figure 4.4 | a) Hole and b) particle state-averaged natural transition orbitals involved in the transitions of the four lowest excited states calculated at the CAM-B3LYP/ANO-S-VDZP level of theory. Isovalue=0.05

From the discussion so far, ω B97X-D and CAM-B3LYP seem to be the most suitable functionals for studying the excited states of tetracene. Based on the exciton descriptors, both functionals seem to give similar results, however CAM-B3LYP excitation energies are closer to the ADC(2)-s, EOM-CCSD and CASPT2(12,12) values (see Table 4.1). CAM-B3LYP has been also reported previously as a suitable functional for the study of tetracene.[21, 27, 40, 41] For studying clusters of N tetracene molecules, where CT between the monomers can occur, ω B97X-D and CAM-B3LYP would be proper choices. Both are long range

corrected functionals, and they have showed a better performance when describing CT excitations.[42, 43]

4.4.2. TETRACENE PAIRS IN THE CRYSTAL STRUCTURE

The trimeric structure highlighted in Fig. 4.5 was taken from an optimised crystal structure, where three different repeating pairs of tetracene molecules were identified and named as AB, AC and BC for the upcoming discussion. Electronic couplings between the photoexcited S_0S_1 state and the 1TT state were calculated using the NOCI approach as described in section 4.2.2 for the three pairs of molecules. Results in Table 4.4 indicate that the electronic coupling is enhanced when the CT states are allowed to mix with the S_1 and 1TT states, which supports the superexchange-mediated mechanism as reported previously for tetracene.[11, 44] The AB pair has the highest electronic coupling (≈ 14 meV), BC has the lowest (≈ 0 meV) and the AC value lies between the other two (≈ 5 meV). As it was discussed in section 4.2.2, the SF probability is proportional to the electronic coupling according to the Fermi's golden rule,[28] suggesting that the AB pair shows the highest SF probability and the BC pair the lowest. Here we present an excited state analysis to provide detailed insights into the nature of the excited states for these pairs, having different relative orientations and electronic couplings, to identify whether there is any relation between the calculated electronic coupling and the character of the involved excited states.

Table 4.4 | Electronic couplings (in meV) between the (diabatic) states $S[1]/^1TT$ for the tetracene pairs AB, AC and BC. In the primed wave functions the CT states were allowed to mix with the $S[1]$ and 1TT states.

Pair	$\Psi_{S[1]}/\Psi_{^1TT}$	$\Psi'_{S[1]}/\Psi'_{^1TT}$
AB	0.6	13.8
AC	0.3	5.2
BC	0.1	0.1

As for the monomer, we observe for all pairs a smooth and systematic blueshift in the excitation energies when increasing the amount of HF exchange (see Table 4.10). No artificial low-lying CT states was observed for the three pairs which means that TD-DFT can be used safely. The exciton descriptors computed at the CAM-B3LYP/ANO-S-VDZP level of theory for the AB, AC and BC pairs are presented in Table 4.5. Exciton descriptors calculated with ω B97X-D are shown in Table 4.11. The fragmentation scheme used to calculate ω_{CT} in the tetracene pairs is shown in Figure 4.6. We observed that for all states in the three pairs $\Omega = 1$ (omitted in Table 4.5) which indicates a pure single excitations character and arise from TD-DFT considering only single excitation and no double or higher excitations. The interested reader is referred to Ref. [13] for how to identify and study the effect of higher excitations.

Differences between the pairs with large electronic coupling (AB and AC) and the pair with zero electronic coupling (BC) start to be evident when analyzing the remaining exciton descriptors in Table 4.5. For the AB pair, S_1 shows a CT character since $d_{h \rightarrow e} = 3.582 \text{ \AA}$ and $\omega_{CT} = 0.90$. The fact that $\omega_{CT} < 1$ indicates that the state has no pure CT

Figure 4.5 | Trimer arrangement highlighted within the tetracene optimised crystal structure, where three pairs of molecules (AB, AC and BC) are identified.

Table 4.5 | Exciton descriptors for the tetracene pairs (AB, AC and BC) calculated at the CAM-B3LYP/ANO-S-VDZP level of theory. CT = charge transfer and CR = charge resonance states. V refers to calculated electronic coupling between the $|S_0S_1\rangle$ and $|^1TT\rangle$ states for each pair.

Pair	V (meV)	State	ΔE (eV) (f)	$d_{h \rightarrow e}$ (Å)	d_{exc} (Å)	ω_{CT}	σ_h (Å)	σ_e (Å)	R_{eh}	NTO transition	Character
AB	14	S_1	2.90(0.058)	3.582	6.205	0.90	3.700	3.700	0.062	$h_1 \rightarrow e_1$	CT state
		S_2	3.06(0.062)	0.029	4.652	0.62	4.108	4.168	0.368	$h_2 \rightarrow e_1$	$\pi \rightarrow \pi^*$
		S_3	3.12(0.137)	1.044	5.240	0.72	3.995	4.172	0.209	$h_1 \rightarrow e_2$	$\pi \rightarrow \pi^*$
										$h_2 \rightarrow e_2$	
		S_4	3.69(0.002)	1.994	5.355	0.77	3.303	4.097	0.111	$h_2 \rightarrow e_2$	CT state
AC	5	S_1	2.91(0.041)	3.915	6.326	0.93	3.350	3.859	0.055	$h_1 \rightarrow e_1$	CT state
		S_2	3.06(0.063)	0.070	4.700	0.62	3.944	4.004	0.301	$h_2 \rightarrow e_1$	$\pi \rightarrow \pi^*$
		S_3	3.10(0.154)	0.702	5.039	0.68	3.935	4.186	0.246	$h_2 \rightarrow e_1$	
										$h_1 \rightarrow e_2$	$\pi \rightarrow \pi^*$
		S_4	3.66(0.002)	2.680	5.726	0.83	3.761	4.022	0.156	$h_2 \rightarrow e_2$	CT state
BC	0	S_1	3.05(0.307)	0.000	4.635	0.61	4.498	4.552	0.475	$h_1 \rightarrow e_1$	$\pi \rightarrow \pi^*$
										$h_2 \rightarrow e_2$	
		S_2	3.12(0.000)	0.000	4.668	0.62	4.525	4.580	0.474	$h_1 \rightarrow e_2$	$\pi \rightarrow \pi^*$
										$h_2 \rightarrow e_1$	
		S_3	3.53(0.000)	0.003	7.389	0.98	4.432	4.487	-0.373	$h_2 \rightarrow e_2$	CR state
		S_4	3.53(0.000)	0.003	7.500	1.00	4.435	4.488	-0.413	$h_1 \rightarrow e_1$	CR state
										$h_2 \rightarrow e_1$	

character, but rather is mixed with the local excited states which lie very close in energy. d_{exc} for S_1 matches with the distance of separation between the tetracene molecules in the AB pair (3.819 Å) suggesting that the electron and hole are located each in a different tetracene molecule. This opposite localisation of the hole and electron in the

pair arrangement is also reflected in the large d_{exc} (6.205 Å). The low positive value of $R_{eh} = 0.062$ can be also interpreted as a loosely Coulombic attraction between the electron and hole which are located at a large distance of separation. Interestingly, the sizes of the electron and hole are the same ($\sigma_e = \sigma_h$). For S_4 the interpretation is not as straightforward as for S_1 ; firstly, $\omega_{CT} = 0.77$ indicates a CT state substantially mixed with the local excitations, which leads to a lowering of the $d_{h \rightarrow e}$ to 1.994 Å and d_{exc} to 5.355 Å and an increase in the electron-hole correlation of $R_{eh} = 0.111$. In contrast, S_2 is a local excited state with $\omega_{CT} = 0.62$ where some CT is occurring; this CT is reflected in the almost zero value of $d_{h \rightarrow e}$. Both, $d_{h \rightarrow e} \approx 0$ and low d_{exc} value (4.652 Å) indicate a local excitation in a single tetracene molecule. The fact that electron and hole are located in the same molecule is reflected in a larger positive R_{eh} (0.368) understood as a stronger Coulombic attraction. For S_3 , the state is considered as a local excitation ($\omega_{CT}=0.72$) in one of the tetracene molecules where the CT mixing is enhanced in comparison with the S_2 state which leads to a higher d_{exc} (1.044 Å) and a lower R_{eh} (0.209).

A very similar interpretation as in AB can be made for the AC pair, where basically the same behaviour can be observed for the four states with S_1 and S_4 as predominantly CT states ($d_{h \rightarrow e} > 2.0$ Å), while S_2 and S_3 are local excitons ($d_{h \rightarrow e} < 1.0$ Å) with some CT character. Larger d_{exc} values indicate CT states and lower d_{exc} local excited states. Although positive R_{eh} values indicate joint excitons in the four states, the lower values for the CT states when compared to the local excitations reveal that the spatial correlation is less pronounced. This indicates that the electron and hole in the CT states are loosely correlated due to their long exciton length.

For the BC pair, with zero electronic coupling, the state order is completely different than for AC and AB. All states have $d_{h \rightarrow e} = 0$ which suggest local excitation character, but just S_1 and S_2 can be identified as excitons due to their lower ω_{CT} values (≈ 0.6) and the relative high positive R_{eh} values (≈ 0.47). The larger R_{eh} values for the local excitations in pair BC suggest a stronger Coulombic attraction of the hole and electron, than in the AB and AC pairs. S_3 and S_4 states can be identified as CR states, due to their ω_{CT} values close to one and the negative R_{eh} values.[25] The $d_{h \rightarrow e} = 0.003$ for both states can be explained due to the parallel symmetry of the pair arrangement. The difference between the states is also reflected in d_{exc} where the CR states have higher values (> 7 Å) than the excitonic states (< 4.7 Å).

The electron-hole correlation plots of the three pairs are depicted in Fig. 4.6, and the state-averaged NTO pairs involved in the transitions are shown in Fig. 4.7. These tools give a more detailed insight on the excited states of the tetracene pairs. For AB and AC pairs, the CT states S_1 and S_4 correspond to transitions between fragments 2 and 5 (as labelled in Fig. 4.6) which corresponds to the middle part of the tetracene molecules. The CT character of the states is supported by the NTO analysis, e.g., h_1 is noticeably more localised in the middle fragment of one of the molecules whereas e_1 is localised on the central part of the opposite molecule. For S_4 in the AB pair, a small local excitation character is expected. S_4 is composed by two excitations, in both (according to the plots) the hole would be localised in fragment 2 whereas the electron would not be only on fragment 5 but also in fragment 2. A similar analysis holds for S_4 in AC. The localised S_2 and S_3 excited states, correspond to $\pi \rightarrow \pi^*$ transitions. Remarkably, the electron-hole correlation plots suggest that the exciton is localised in one of the molecules in the AB

and AC pairs, which is line with previously reported observations.[2, 9] Additionally, the CT between neighbouring chromophores inferred by the exciton descriptors is confirmed here by the grey off-diagonal elements.

For the BC pair, the S_1 and S_2 states correspond both to excitations delocalised in both monomers equally, which differs from the local exciton in the AB and AC pairs. Small CT contributions are predicted for these states. Both states are composed of two transitions (both of $\pi \rightarrow \pi^*$ character) as stated in Table 4.5, where the NTOs reveal that the orbitals are delocalised in the middle fragments of both molecules.

Figure 4.6 | Labeled fragmentation scheme and electron-hole correlation plots for the three tetracene pairs of molecules AB, AC and BC calculated at the CAM-B3LYP/ANO-S-VDZP level of theory. e and h represent the electron and hole coordinates, respectively.

The exciton descriptors confirm that the AB and AC pairs, with non-zero electronic couplings, have low-lying CT states close in energy to the local excited states. $d_{h \rightarrow e}$ values and the electron-hole correlation plots in Figure 4.6 show that there is mixing between these states for AB and AC pairs. This supports the CT-mediated superexchange mechanism inferred by the enhancement of electronic couplings when CT states are

Figure 4.7 | State-averaged natural transition orbitals involved in the five lowest singlet excited states for the pairs AB, AC and BC calculated at the CAM-B3LYP/ANO-S-VDZP level of theory. Isovalues = 0.05.

mixed with the S_1 and 1TT states in these two pairs. Results obtained with the ω B97X-D functional (Table 4.11 and Figure 4.10) predict mostly pure local exciton (LE) states, which does not reflect the enhancement of the electronic coupling via CT mixing. In contrast in the BC pair, with zero electronic coupling, high-lying CR states are predicted, which could not be inferred from the electronic coupling study. Based on these observations, the difference in electronic couplings might be then attributed to the presence and mixing in of CT states, while CR states were observed in the pair with zero electronic coupling. Whether CR states play any role in the overall SF process need to be clarified and studied further. More important for the SF process, that is the focus of this work, are the interesting trends observed for the electron-hole correlation coefficient, R_{eh} ; for the AB and AC pairs the local excitations (S_2 and S_3) are expected to have a weaker Coulombic attraction ($R_{eh} = 0.36$ and 0.209 for AB, $R_{eh} = 0.301$ and 0.246 for AC) in comparison with the local excitations (S_1 and S_2) in pair BC ($R_{eh} \approx 0.47$). We speculate that the excited electron could be more easily transferred to a neighbouring molecule in pairs AB and AC, due to the weaker Coulombic attraction. This might facilitate the CT-mediated superexchange mechanism for the formation of the 1TT state from the photoexcited molecule (see Figure 4.1).

4.5. CONCLUSIONS

In this study we have performed an excited state analysis on the tetracene molecule, in its monomeric and dimeric to identify the role of CT states in the underlying mechanism through which the SF process occurs.

Our study revealed that the CAM-B3LYP functional shows the best overall agreement in terms of excitation energies and exciton descriptors, based on the one-particle transition density matrix, when compared with the wave function-based methods ADC(2)-s and EOM-CCSD, and therefore used as the most suitable and computationally affordable methodology to further study tetracene pairs. The dependency of the fragmentation scheme in the interpretation of results was explored; a symmetrical fragmentation for acenes is suggested for further studies when possible. In the particular case of tetracene, a three-units fragmentation scheme was presented and explored.

4

Exciton descriptors, electron-hole correlation plots, and NTOs were computed for three pairs of tetracene molecules, with different relative orientations and electronic couplings, and then used to assign the character of their excited states. Our results show that the exciton descriptors can differentiate between CT and CR states. The presence of low-lying CT states, mixed with the local excitations, are found in pairs with non-zero electronic coupling (AB and AC) which indicates that the conversion to the 1TT states is enhanced and most probably occur through a CT-mediated superexchange mechanism. Relatively high-lying CR states are observed in the pair with zero electronic coupling (BC). Moreover, we have found that excitons in AB and AC pairs have a weaker Coulombic attraction (indicated by their lower electron-hole correlation coefficient) than the exciton in the BC pair, and therefore they might easily undergo through SF conversion to the 1TT state.

In summary, our work has shown the applicability of the excited state analysis to characterize the excited states of the tetracene pairs, with different relative orientation and electronic coupling, and to differentiate the role that CT and CR states play in the underlying mechanism of the SF process. The analysis can be extended to study the influence of vibrational modes and environmental effects in the electronic couplings and the excited states of the tetracene pairs or other potential molecules exhibiting SF of comparable size and complexity.

4.6. APPENDIX

4.6.1. CRYSTAL OPTIMIZATION OF TETRACENE

The crystal structure of tetracene (TETCEN as identifier) was optimized using periodic DFT calculations at the PBE/6-31G(d,p) level of theory, in addition the Grimme dispersion correction was included for the optimization. Only atomic positions were optimized using a $4 \times 4 \times 4$ k-point mesh, followed by a frequency calculation showing that the crystal structure corresponds to a genuine minimum. All of these calculations were performed using the CRYSTAL14 *ab initio* package.[45] The optimization of tetracene led to a genuine minimum (confirmed by the frequencies calculation).

4.6.2. INFLUENCE OF THE BASIS SET IN EXCITON DESCRIPTORS

Tables 4.6, 4.7, 4.8 and 4.9 show the results of basis set influence in the exciton descriptors. Basis set influence can be neglected.

Table 4.6 | Benchmarking for the methodologies using 6-31G as the basis set.

BLYP					B3LYP				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	2.48	0.0662	H to L	$\pi \rightarrow \pi^*$	1	2.78	0.1016	H to L	$\pi \rightarrow \pi^*$
2	3.08	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.60	0.0043	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
3	3.33	0.0035	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	3	3.69	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	3.90	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	4	4.27	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
5	4.14	0.0003	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$	5	4.79	0.0000	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$
BHLYP					CAM-B3LYP				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	3.17	0.1643	H to L	$\pi \rightarrow \pi^*$	1	3.18	0.1575	H to L	$\pi \rightarrow \pi^*$
2	3.86	0.0074	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.84	0.0056	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
3	4.53	0.0000	H-2 to L	$\pi \rightarrow \pi^*$	3	4.54	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
4	4.72	0.0000	H to L+2	$\pi \rightarrow \pi^*$	4	4.70	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
5	5.42	0.0000	H-4 to L, etc.	$\pi \rightarrow \pi^*$	5	5.37	0.0000	H-4 to L, etc.	$\pi \rightarrow \pi^*$
ω B97X-D					ADC(2)-s				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	3.25	0.1678	H to L	$\pi \rightarrow \pi^*$	1^1B_{2u}	3.24	0.1121	H to L	$\pi \rightarrow \pi^*$
2	3.87	0.0055	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	1^1B_{3u}	3.72	0.0044	H-2 to L, etc.	$\pi \rightarrow \pi^*$
3	4.65	0.0000	H-2 to L	$\pi \rightarrow \pi^*$	1^1B_{1g}	4.62	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	4.80	0.0000	H to L+2	$\pi \rightarrow \pi^*$	2^1B_{1g}	4.83	0.0000	H to L+1, H-1 to L	$\pi \rightarrow \pi^*$
5	5.37	0.0000	H-4 to L, etc.	$\pi \rightarrow \pi^*$	2^1A_g	5.22	0.0000	H-7 to L, H-1 to L+2, etc.	$\pi \rightarrow \pi^*$
ADC(2)-x					ADC(3)				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
2^1A_g	2.53	0.0000	H-8 to L, H to L+6, ...	$\pi \rightarrow \pi^*$	2^1A_g	2.64	0.0000	NA	$\pi \rightarrow \pi^*$
1^1B_{2u}	2.68	0.0910	H to L	$\pi \rightarrow \pi^*$	1^1B_{2u}	3.24	0.1153	H to L	$\pi \rightarrow \pi^*$
1^1B_{3u}	2.73	0.0030	H-6 to L, H to L+3	$\pi \rightarrow \pi^*$	1^1B_{3u}	3.28	0.0038	H-5 to L, H to L+5, ...	$\pi \rightarrow \pi^*$
1^1B_{1g}	3.48	0.0000	H-3 to L, H to L+1	$\pi \rightarrow \pi^*$	2^1B_{3u}	4.02	0.0000	H-1 to L+7, H-8 to L+1	$\pi \rightarrow \pi^*$
2^1B_{3u}	3.84	0.0003	H-9 to L, H-8 to L+1,...	$\pi \rightarrow \pi^*$	1^1B_{1g}	4.26	0.0000	H-1 to L, H to L+1,...	$\pi \rightarrow \pi^*$

Table 4.7 | Benchmarking for the methodologies using 6-311G as the basis set.

BLYP					B3LYP				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	2.45	0.0656	H to L	$\pi \rightarrow \pi^*$	1	2.75	0.1002	H to L	$\pi \rightarrow \pi^*$
2	3.07	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.58	0.0020	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
3	3.31	0.0016	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	3	3.67	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	3.87	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	4	4.23	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
5	4.11	0.0001	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$	5	4.75	0.0000	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$
BHLYP					CAM-B3LYP				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	3.15	0.1623	H to L	$\pi \rightarrow \pi^*$	1	3.14	0.1554	H to L	$\pi \rightarrow \pi^*$
2	3.85	0.0043	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.81	0.0024	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
3	4.52	0.0000	H-2 to L	$\pi \rightarrow \pi^*$	3	4.52	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
4	4.69	0.0000	H to L+2	$\pi \rightarrow \pi^*$	4	4.64	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
5	5.40	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$	5	5.34	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$
ω B97X-D					ADC(2)-s				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	3.21	0.1664	H to L	$\pi \rightarrow \pi^*$	1 ¹ B _{2u}	3.18	0.1100	H to L	$\pi \rightarrow \pi^*$
2	3.84	0.0026	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	1 ¹ B _{3u}	3.67	0.0036	H-2 to L, H to L+2, ...	$\pi \rightarrow \pi^*$
3	4.62	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	1 ¹ B _{1g}	4.55	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	4.76	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	2 ¹ B _{1g}	4.73	0.0000	H to L+1, H-1 to L	$\pi \rightarrow \pi^*$
5	5.34	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$	2 ¹ A _g	5.16	0.0000	H-6 to L, H-1 L+2,...	$\pi \rightarrow \pi^*$
ADC(2)-x									
State	VEE(eV)	f	Transition	Nature					
2 ¹ A _g	2.53	0.0000	H-7 to L, H to L+9,...	$\pi \rightarrow \pi^*$					
1 ¹ B _{2u}	2.63	0.0895	H to L	$\pi \rightarrow \pi^*$					
1 ¹ B _{3u}	2.70	0.0022	H-5 to L, H to L+7	$\pi \rightarrow \pi^*$					
1 ¹ B _{1g}	3.45	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$					
2 ¹ B _{3u}	3/83	0.0007	H-8 to L, H-7 to L+1	$\pi \rightarrow \pi^*$					

Table 4.8 | Benchmarking for the methodologies using cc-pVDZ as the basis set.

BLYP					B3LYP				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	2.36	0.0576	H to L	$\pi \rightarrow \pi^*$	1	2.64	0.0870	H to L	$\pi \rightarrow \pi^*$
2	3.01	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.49	0.0027	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
3	3.23	0.0022	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	3	3.60	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	3.78	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	4	4.13	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
5	4.03	0.0001	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$	5	4.66	0.0000	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$
BHLYP					CAM-B3LYP				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	3.03	0.1374	H to L	$\pi \rightarrow \pi^*$	1	3.01	0.1330	H to L	$\pi \rightarrow \pi^*$
2	3.73	0.0033	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.72	0.0034	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
3	4.42	0.0000	H-2 to L	$\pi \rightarrow \pi^*$	3	4.42	0.0000	H-2 to L	$\pi \rightarrow \pi^*$
4	4.60	0.0000	H to L+2	$\pi \rightarrow \pi^*$	4	4.56	0.0000	H to L+2	$\pi \rightarrow \pi^*$
5	5.29	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$	5	5.25	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$
ω B97X-D					ADC(2)-s				
State	VEE(eV)	f	Transition	Nature	State	VEE(eV)	f	Transition	Nature
1	3.07	0.1414	H to L	$\pi \rightarrow \pi^*$	1 ¹ B _{2u}	2.91	0.0952	H to L	$\pi \rightarrow \pi^*$
2	3.75	0.0034	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	1 ¹ B _{3u}	3.56	0.0017	H-2 to L, H to L+2, ...	$\pi \rightarrow \pi^*$
3	4.49	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	1 ¹ B _{1g}	4.30	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	4.69	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	2 ¹ B _{1g}	4.48	0.0000	H to L+1, H-1 to L	$\pi \rightarrow \pi^*$
5	5.25	0.0000	H-4 to L, H-2 to L+1, ...	$\pi \rightarrow \pi^*$	2 ¹ B _{3u}	4.97	3.1742	H to L+2, H-2 to L	$\pi \rightarrow \pi^*$
ADC(2)-x									
State	VEE(eV)	f	Transition	Nature					
2 ¹ A _g	2.53	0.0000	H-7 to L, H to L+9,...	$\pi \rightarrow \pi^*$					
1 ¹ B _{2u}	2.63	0.0895	H to L	$\pi \rightarrow \pi^*$					
1 ¹ B _{3u}	2.70	0.0022	H-5 to L, H to L+7	$\pi \rightarrow \pi^*$					
1 ¹ B _{1g}	3.45	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$					
2 ¹ B _{3u}	3.83	0.0007	H-8 to L, H-7 to L+1,...	$\pi \rightarrow \pi^*$					

Table 4.9 | Benchmarking for the methodologies using cc-pVTZ as the basis set.

BLYP					B3LYP				
State	VEE(eV)	<i>f</i>	Transition	Nature	State	VEE(eV)	<i>f</i>	Transition	Nature
1	2.32	0.0541	H to L	$\pi \rightarrow \pi^*$	1	2.59	0.0807	H to L	$\pi \rightarrow \pi^*$
2	2.99	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.46	0.0016	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$
3	3.21	0.0013	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$	3	3.58	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
4	3.73	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	4	4.07	0.0000	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
5	3.99	0.0000	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$	5	4.60	0.0000	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$
BHLYP					CAM-B3LYP				
State	VEE(eV)	<i>f</i>	Transition	Nature	State	VEE(eV)	<i>f</i>	Transition	Nature
1	2.99	0.1287	H to L	$\pi \rightarrow \pi^*$	1	2.94	0.1219	H to L	$\pi \rightarrow \pi^*$
2	3.71	0.0023	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$	2	3.69	0.0021	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$
3	4.39	0.0000	H-2 to L	$\pi \rightarrow \pi^*$	3	4.37	0.0000	H-2 to L	$\pi \rightarrow \pi^*$
4	4.57	0.0000	H to L+2	$\pi \rightarrow \pi^*$	4	4.49	0.0000	H to L+2	$\pi \rightarrow \pi^*$
5	5.27	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$	5	5.21	0.0000	H-3 to L, H to L+3	$\pi \rightarrow \pi^*$
ω B97X-D									
State	VEE(eV)	<i>f</i>	Transition	Nature					
1	3.01	0.1306	H to L	$\pi \rightarrow \pi^*$					
2	3.72	0.0024	H-1 to L, H to L+1	$\pi \rightarrow \pi^*$					
3	4.44	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$					
4	4.64	0.0000	H-2 to L, H to L+2	$\pi \rightarrow \pi^*$					
5	5.21	0.0000	H-4 to L, H-2 to L+1,...	$\pi \rightarrow \pi^*$					

4.6.3. ADC(2)-s AND EOM-CCSD ORBITALS

Figure 4.8 | a) Hole and b) electron(particle) natural transition orbitals for the ADC(2)-s/ANO-S-VDZP and EOM-CCSD/ANO-S-VDZP levels of theory for the tetracene molecule.

4.6.4. ADDITIONAL FRAGMENTATION SCHEMES FOR TETRACENE

Figure 4.9 | Different asymmetric and symmetric fragmentations of the tetracene and their corresponding electron-hole correlation plots.

4.6.5. DFT ANALYSIS FOR THE TETRACENE PAIRS

The excitation energies and oscillator strengths calculated with different functionals using ANO-S-VDZP as basis set for the four lowest singlet excited states of the AB, AC and BC pairs are given in Table 4.10. For all pairs a smooth and systematic blueshift is observed, when increasing the the amount of Hartree Fock exchange which suggests these states do not have strong CT character and TD-DFT can be used.

Table 4.10 | Excitation energies (in eV) and oscillator strengths (in parentheses) for the four lowest singlet excited states for pairs AB, AC and BC of tetracene molecules calculated with different functionals. ANO-S-VDZP used as basis set. Calculated electronic coupling for each pair is indicated.

Pair	V(meV)	State	BLYP	B3LYP	BHLYP	ω B97X-D	CAM-B3LYP
AB	14	S ₁	1.33(0.004)	1.91(0.005)	2.88(0.019)	3.08(0.156)	2.90(0.058)
		S ₂	2.00(0.008)	2.58(0.046)	3.08(0.063)	3.13(0.071)	3.06(0.062)
		S ₃	2.38(0.027)	2.68(0.042)	3.12(0.180)	3.29(0.047)	3.12(0.137)
		S ₄	2.58(0.000)	2.76(0.077)	3.72(0.000)	3.73(0.000)	3.69(0.002)
AC	4	S ₁	1.33(0.004)	1.91(0.005)	2.88(0.014)	3.08(0.126)	2.91(0.041)
		S ₂	2.00(0.002)	2.59(0.026)	3.08(0.060)	3.13(0.103)	3.06(0.063)
		S ₃	2.37(0.036)	2.68(0.066)	3.11(0.188)	3.25(0.046)	3.10(0.154)
		S ₄	2.40(0.069)	2.74(0.073)	3.71(0.002)	3.73(0.002)	3.66(0.002)
BC	0	S ₁	1.68(0.000)	2.34(0.002)	3.07(0.307)	3.11(0.326)	3.05(0.307)
		S ₂	1.68(0.001)	2.34(0.000)	3.14(0.000)	3.18(0.000)	3.12(0.000)
		S ₃	2.34(0.131)	2.67(0.199)	3.50(0.000)	3.73(0.004)	3.53(0.000)
		S ₄	2.41(0.000)	2.72(0.000)	3.50(0.000)	3.74(0.000)	3.53(0.000)

4.6.6. EXCITON ANALYSIS FOR THE AB, AC AND BC TETRACENE PAIRS AT THE ω B97X-D/ANO-S-VDZP LEVEL OF THEORY

Table 4.11 | Exciton descriptors for the tetracene pairs of molecules (AB, AC and BC) calculated at the ω B97X-D/ANO-S-VDZP level of theory. CT = charge transfer and LE = local exciton states.

Pair	State	Ω	$d_{h \rightarrow e}(\text{\AA})$	$d_{exc}(\text{\AA})$	ω_{CT}	$\sigma_h(\text{\AA})$	$\sigma_e(\text{\AA})$	R_{eh}	Character
AB	S_1	1	1.147	5.110	0.70	3.306	4.012	0.084	LE
	S_2	1	0.086	4.348	0.62	3.418	3.431	0.090	LE
	S_3	1	3.294	5.991	0.88	3.468	3.961	0.097	CT
	S_4	1	0.043	4.147	0.61	3.260	3.347	0.212	LE
AC	S_1	1	1.147	5.110	0.70	3.306	4.012	0.084	LE
	S_2	1	0.086	4.620	0.62	3.418	3.431	0.090	LE
	S_3	1	3.924	5.991	0.88	3.418	3.431	0.090	CT
	S_4	1	0.043	4.147	0.61	3.260	3.347	0.212	LE
BC	S_1	1	0.000	4.525	0.60	4.474	4.525	0.494	LE
	S_2	1	0.000	4.555	0.61	4.500	4.554	0.494	LE
	S_3	1	0.000	4.375	0.63	4.424	4.494	0.519	LE
	S_4	1	0.000	4.130	0.61	4.431	4.498	0.572	LE

Figure 4.10 | Labeled fragmentation scheme and electron-hole correlation plots for the three tetracene pairs of molecules AB, AC and BC calculated at the ω B97X-D/ANO-S-VDZP level of theory. e and h represent the electron and hole coordinates, respectively.

4.6.7. BENCHMARKING OF EXCITED STATE DESCRIPTORS FOR TETRACENE PAIRS AB, AC AND BC USING DIFFERENT FUNCTIONALS

Table 4.12 | Excited-state descriptors benchmarking for pair of tetracene molecules AB

Pair	Method	State	$\Delta E(\text{eV})$	f	Ω	d_{exc}	$d_{h \rightarrow e}$	σ_h	σ_e	R_{eh}
AB	BLYP	S ₁	1.339	0.004	1	6.860	4.883	3.379	3.431	-0.001
		S ₂	2.003	0.008	1	6.828	4.743	3.429	3.497	-0.006
		S ₃	2.387	0.028	1	5.406	0.023	4.230	4.281	0.193
		S ₄	2.418	0.074	1	5.476	0.131	4.229	4.269	0.170
		S ₅	2.595	0.001	1	7.077	4.743	3.839	3.465	-0.032
	B3LYP	S ₁	1.913	0.005	1	6.768	4.810	3.367	3.422	0.016
		S ₂	2.577	0.046	1	6.317	3.341	3.726	3.941	0.023
		S ₃	2.683	0.043	1	5.084	0.046	4.211	4.270	0.281
		S ₄	2.764	0.077	1	5.667	1.448	4.143	4.157	0.128
		S ₅	3.356	0.000	1	6.536	4.436	3.878	3.553	0.168
	BHLYP	S ₁	2.891	0.019	1	6.512	4.473	3.402	3.434	0.041
		S ₂	3.095	0.064	1	4.559	0.031	4.003	4.037	0.357
		S ₃	3.132	0.180	1	4.751	0.296	3.953	4.069	0.301
		S ₄	3.727	0.000	1	4.251	0.161	3.418	3.573	0.262
		S ₅	3.733	0.002	1	4.188	0.079	3.424	3.446	0.257
	CAM-B3LYP	S ₁	2.908	0.058	1	6.191	3.544	3.718	3.698	0.063
		S ₂	3.064	0.063	1	4.656	0.034	4.103	4.162	0.365
		S ₃	3.127	0.136	1	5.250	1.062	3.977	4.172	0.205
		S ₄	3.691	0.002	1	5.491	2.262	3.316	4.113	0.105
		S ₅	3.713	0.001	1	4.337	0.166	3.652	3.648	0.295

Table 4.13 | Excited-state descriptors benchmarking for pair of tetracene molecules AC

Pair	Method	State	$\Delta E(\text{eV})$	f	Ω	d_{exc}	$d_{h \rightarrow e}$	σ_h	σ_e	R_{eh}
AC	BLYP	S_1	1.339	0.004	1	6.982	5.056	3.371	3.437	-0.001
		S_2	2.004	0.002	1	7.016	5.034	3.383	3.515	-0.003
		S_3	2.378	0.035	1	5.428	0.371	4.106	4.195	0.149
		S_4	2.402	0.071	1	5.500	0.261	4.158	4.207	0.137
		S_5	2.605	0.002	1	5.500	0.261	4.158	4.207	0.137
	B3LYP	S_1	1.912	0.005	1	6.851	4.930	3.350	3.430	0.015
		S_2	2.589	0.026	1	6.438	3.559	3.394	4.139	-0.004
		S_3	2.678	0.066	1	5.117	0.298	3.750	3.816	0.088
		S_4	2.738	0.073	1	5.665	1.429	3.760	4.237	0.064
		S_5	3.371	0.000	1	6.671	4.778	3.800	3.551	0.199
	BHLYP	S_1	2.887	0.014	1	6.573	4.593	3.287	3.497	0.040
		S_2	2.887	0.014	1	4.598	0.125	4.149	4.212	0.396
		S_3	3.123	0.189	1	4.667	0.160	4.156	4.201	0.377
		S_4	3.723	0.002	1	4.468	0.495	3.954	3.860	0.354
		S_5	3.731	0.000	1	4.257	0.177	3.917	4.021	0.426
	CAM-B3LYP	S_1	2.912	0.042	1	6.319	3.899	3.352	3.862	0.055
		S_2	3.059	0.065	1	4.693	0.072	3.914	3.977	0.293
		S_3	3.107	0.152	1	5.046	0.724	3.903	4.174	0.237
		S_4	3.668	0.002	1	5.802	2.840	3.712	4.005	0.142
		S_5	3.714	0.000	1	4.212	0.041	3.976	4.058	0.451

Table 4.14 | Excited-state descriptors benchmarking for pair of tetracene molecules BC

BC	Method	State	$\Delta E(\text{eV})$	f	Ω	d_{exc}	$d_{h \rightarrow e}$	σ_h	σ_e	R_{eh}
BC	BLYP	S_1	1.684	0.000	1	7.786	0.022	4.556	4.594	-0.448
		S_2	1.684	0.001	1	7.786	0.022	4.556	4.594	-0.448
		S_3	2.383	0.132	1	5.390	0.000	4.647	4.690	0.334
		S_4	2.419	0.000	1	5.432	0.000	4.665	4.710	0.329
		S_5	2.939	0.000	1	7.909	0.005	4.873	4.604	-0.393
	B3LYP	S_1	2.344	0.002	1	7.688	0.091	4.516	4.560	-0.435
		S_2	2.344	0.000	1	7.690	0.091	4.516	4.558	-0.436
		S_3	2.674	0.200	1	5.065	0.000	4.581	4.632	0.396
		S_4	2.724	0.000	1	5.102	0.000	4.602	4.658	0.393
		S_5	3.483	0.000	1	4.628	0.000	4.549	4.60	0.489
	BHLYP	S_1	3.082	0.308	1	4.541	0.000	4.483	4.517	0.491
		S_2	3.152	0.000	1	4.574	0.000	4.512	4.546	0.490
		S_3	3.510	0.000	1	7.495	0.004	4.433	4.471	-0.417
		S_4	3.512	0.000	1	7.534	0.004	4.435	4.472	-0.431
		S_5	3.734	0.000	1	4.125	0.000	4.412	4.466	0.568
	CAM-B3LYP	S_1	3.051	0.308	1	4.634	0.000	4.498	4.551	0.475
		S_2	3.119	0.000	1	4.667	0.000	4.524	4.578	0.474
		S_3	3.529	0.000	1	7.393	0.003	4.432	4.485	-0.375
		S_4	3.536	0.000	1	7.498	0.003	4.434	4.487	-0.413
		S_5	3.721	0.000	1	4.204	0.000	4.446	4.511	0.560

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5

INFLUENCE OF CRYSTAL PACKING IN SINGLET FISSION

Singlet Fission?

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ABSTRACT

In previous chapters, we have studied singlet fission (SF) employing pairs of molecules neglecting the surrounding crystal packing, this is the so-called gas phase dimer model. This model has shown its utility to study the process, but it does not always cover all the physics and the effect of the surrounding atoms has to be included in the SF process.

In this chapter, we explore the influence of crystal packing on the electronic couplings, and on the so-called exciton descriptors and electron-hole correlation plots. We have studied three tetracene dimers extracted from the crystal structure, as well as several dimers and trimers of the α and β polymorphs of 1,3-diphenylisobenzofuran (DPBF). These polymorphs show different SF yields. Our results highlight that the character of the excited states of tetracene depends on both the mutual disposition of molecules and inclusion of the environment. The latter does however not change significantly the interpretation of the SF mechanism in the studied systems. For DPBF, we establish how the excited state analysis is able to pinpoint differences between the polymorphs. We observe strongly bound correlated excitons in the β polymorph which might hinder the formation of the 1TT state and, consequently, explain its low SF yield.

5

5.1. INTRODUCTION

Singlet fission (SF) takes place typically in organic solids and a general scheme is depicted in Figure 5.1. In this process, a singlet excited (S_1) chromophore, generated upon absorption of a single photon by the molecule in its ground state (S_0), transfers part of its energy to a neighbour chromophore to form two coupled triplets (the so-called 1TT state) in an overall spin-allowed process.[1, 2] The conversion efficiency to the 1TT state depends mainly on two factors; First, the SF process should be preferably slightly exothermic (although endothermic SF has also been investigated[3, 4]) which means that the energy condition $\Delta E(S_1) > 2\Delta E(T_1)$ has to be fulfilled for the individual chromophore. Second, the mutual disposition of the chromophores plays an essential role in both the energy levels and the electronic coupling between the relevant diabatic states. Theoretical efforts, at different levels of sophistication, have been made to find novel chromophores that fulfil the SF energy condition[5–11] as well as protocols to optimise the spatial distribution of the chromophores and maximise the coupling between S_0S_1 (or S_1S_0) and 1TT . [12–15]

The simple picture in Figure 5.1 is generally accepted, but the conversion from S_0S_1 (or S_1S_0) to the 1TT state is still subject of ongoing debate. Three different mechanisms have been proposed to explain the process:[16–20] (i) the direct mechanism in which there is straight conversion via a two-electron transfer; (ii) the mediated mechanism, in which high-energy charge transfer (CT) states (D^+D^- and D^-D^+ in Figure 5.1) are believed to mix with the initial and final states enhancing their coupling through the so-called superexchange effect; and finally (iii) a two-step mechanism known as charge

Figure 5.1 | Singlet fission process: Upon absorption of a photon, one photoexcited (S_1) chromophore transfers part of its energy to a neighbour in the ground state (S_0) to form two coupled triplets (1TT) in a spin-allowed process. Charge transfer states (D^-D^+ and D^+D^-) are believed to play an essential role.

hopping in which CT states act as intermediates and are populated before the generation of the 1TT state. Thus, understanding how the coupled triplets are generated is crucial to design guidelines for optimising the conditions for the formation of the 1TT state.

Several theoretical and computational studies have been performed to understand the underlying mechanism of SF. These works focus either on the simple model of two interacting chromophores in the gas phase[13, 17, 21–25] or by studying the process taking into account the crystal packing applying a variety of methods.[26–29] The gas phase dimer model has been proven to be useful as a first approximation to study SF. However, its reliability for the description of the process in organic crystals needs further analysis and validation.

An early study on the acenes family employing a simple kinetic model[22] has pointed out that the SF yield depends on different factors, such as couplings, singlet-triplet energy gaps and entropic factors with the latter being an important contribution to be considered. A previous study on pentacene J-type and H-type ring-shaped aggregates have concluded that the electronic coupling depends heavily on both the size and structure of the aggregate.[30] These findings show the importance of going beyond the dimer model. Furthermore, the influence of the environment has been studied previously in model crystals for tetracene and pentacene. The findings suggest that SF can occur without the presence of a low-lying CT state in the acene crystal and that for tetracene the 1TT state is higher in energy than S_1 and S_2 . [31] Nevertheless, a recent work has pointed to the presence of low-lying CT states in pentacene clusters that are energetically available when increasing the cluster size and that depend on the choice of functional.[32] These conclusions encourage to study the SF process taking into account the crystal environment.

Here, we present a study of the influence of crystal packing on the electronic couplings, the so-called exciton descriptors and the overall underlying SF mechanism on pairs of tetracene[33–37] and 1,3-diphenylisobenzofuran (DPBF),[25, 38–40] two chromophores known to exhibit SF. This contribution is organized as follows: the approach employed to

evaluate the electronic couplings for the pairs of molecules is presented in Section 5.1.1. In Section 5.1.2, a subset of the so-called exciton descriptors and how to apply them to assign the character of excited states is described. The approaches used for the inclusion of the environment are mentioned in each of these sections. Results of the influence of the environment on the electronic couplings and exciton descriptors for pairs of the two different chromophores are discussed in Section 5.3. Concluding remarks of this contribution are given in Section 5.4.

5.1.1. NON-ORTHOGONAL CONFIGURATION INTERACTION APPROACH

A SF rate (k_E) in a system can be approximated by means of Fermi's golden rule:[41]

$$k_E = \frac{2\pi}{\hbar} |V|^2 \rho(E) \quad (5.1)$$

where V denotes the electronic coupling between the relevant diabatic states and $\rho(E)$ represents the density of states per energy (E) unit. Different approaches have been used to evaluate the electronic coupling,[1, 2, 12, 42–44] but in this work a non-orthogonal configuration interaction (NOCI) approach is employed.[45, 46] The advantages of using this method include a clear chemical interpretation of the states and the compactness of wave functions since each of the molecular states are described with its own optimal set of orbitals.[47]

The NOCI wave function describing the molecular pair can be expanded as a linear combination of the so-called many-electron basis functions (MEBFs, Φ) which describe different electronic states of the pair. These MEBFs are generated as antisymmetrised products of molecular wave functions:

$$|\Phi_\mu\rangle = \sum_\sigma \kappa_\sigma \hat{A} \prod_A^N |\Psi_A^I\rangle_\sigma \quad (5.2)$$

where α and β represent the electronic states of molecules A and B , respectively, and N is the number of molecules in system, κ_σ are the corresponding spin-coupling coefficients and summation over σ denotes that anti symmetrized products of the molecular wave functions (with different M_S) can be combined leading to MEBFs that are spin eigenfunctions. In this contribution, the molecular wave functions are chosen to be of the complete active space self-consistent field (CASSCF) type. For the SF process, the following six electronic states are of particular interest: $\Phi_{S_0S_0}$, $\Phi_{S_0S_1}$, $\Phi_{S_1S_0}$, Φ_{1TT} , $\Phi_{D^+D^-}$ and $\Phi_{D^-D^+}$. Subsequently, Hamiltonian and overlap matrix elements between the MEBFs are calculated. The electronic coupling can be then computed by the means of the direct coupling scheme:[48]

$$V = \frac{\langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle - \frac{1}{2} (\langle \Phi_\mu | \hat{H} | \Phi_\mu \rangle + \langle \Phi_\nu | \hat{H} | \Phi_\nu \rangle) \cdot \langle \Phi_\mu | \Phi_\nu \rangle}{1 - \langle \Phi_\mu | \Phi_\nu \rangle^2} \quad (5.3)$$

where μ and the ν represent the local excited states and the 1TT state, respectively. We use the embedded cluster approach[49, 50] to account for the surrounding crystal environment. The orbital optimisation and generation of the molecular wave functions

of the electronic states of the molecules are performed using a frozen Hartree-Fock (HF) electron density around the target molecule. Further details on how the frozen density is generated are explained in Section 5.2.

5.1.2. EXCITON DESCRIPTORS

In addition to the excited state of local singlet coupled triplets, there are four more states that can play a role in the basic description of the singlet fission process. The character of these states is depicted in Figure 5.2.[51] Two of them correspond to local excitons on each of the chromophores (S_0S_1 and S_1S_0) and the other two are separated CT states (D^+D^- and D^-D^+). Linear combinations of these states can be constructed under resonance conditions, leading to excitonic resonance (ER) and charge resonance (CR) states.[51] Please note that the presence of LE states in the dimer excludes the ER states (and vice-versa), and similar for the CT and CR states that are also mutually exclusive. An excited state analysis can be done in order to identify and differentiate between the state character.

Figure 5.2 | Localised excited states and their linear combinations leading to delocalised states in the pair model.

Recently developed excited state analysis based on the one-particle transition density matrix (1TDM) offers a compact description of the character of electronic transitions.[52, 53] This analysis has the following advantages:[54] (1) it can be applied to any excited state method that provides access to the 1TDM, (2) allows a detailed benchmarking of excited state methods, and (3) facilitates the characterisation of excited states of a molecule or a cluster of molecules. The character assignment can be done based on the so-called exciton descriptors.[51, 55–59] In a previous work, we have compared a subset of these descriptors calculated with time-dependent density functional theory (TD-DFT) against wave function-based methods for the tetracene molecule and pairs, establishing CAM-B3LYP/ANO-S-VDZP as the most suitable theoretical method.[60] Here, we will focus on describing the exciton descriptors depicted in panel (a) of Figure 5.3 and how these can be used to assign the character of excited states. For a more elaborate discussion on

excited-state descriptors, the reader is referred to the Refs. 52–54.

Figure 5.3 | a) Depiction of the subset of exciton descriptors employed in this contribution, and b) general representation of the *electron-hole* correlation plots with a fragmentation scheme of $n = 4$ as an example.

A descriptor related to the amount of CT character in an excited state is the vectorial distance ($d_{h \rightarrow e}$) between the centroids of the hole and electron. This quantity is particularly useful to identify CT states: $d_{h \rightarrow e} \approx 0$ indicate a locally excited (LE) state whereas $d_{h \rightarrow e} > 0$ indicates a completely separated CT state. The magnitude of $d_{h \rightarrow e}$ (in Å) can be often associated with the distance of separation between the fragments where the CT takes place, e.g., it can be close to the distance of separation between the chromophores if the CT occurs in a pair of molecules.

Detection of CR states can be challenging but the exciton size (d_{exc}) has been proven to be helpful in their characterisation.[51] This descriptor is the root-mean-square distance between the hole and electron, and takes into account not only the separation between the centroids of hole and electron but also their spatial distribution as well as their covariance.[54] It is advisable to look at this descriptor to identify hidden resonance states, e.g. d_{exc} values for ER and CR states are rather different and easily spotted by comparison.

R_{eh} is known as the correlation coefficient and its value ranges from -1 to 1. Its sign provides information about the exciton correlation. Positive values indicate that the hole and electron are attracted to each other by Coulombic forces and that they move together as an entity. On the contrary, negative values suggest that the electron and hole avoid each other in space arising from exchange repulsion or correlation effects.[59] If its value is zero, there is no correlation between the hole and the electron, and they move independently from each other.

Electron-hole correlation plots are pseudo-matrix representations of the so-called charge transfer numbers (Ω_{AB}). Ω_{AB} are calculated between *a priori* defined fragments in which the molecule or system is split. Panel (b) of Figure 5.3 shows a 4×4 *electron-hole* correlation plot of a system split into four fragments. Local excitations correspond to the diagonal elements of the matrix going from the bottom-left to upper-right, whereas off-diagonal elements represent CT occurring between the corresponding fragments. In this contribution, the intensity of the transition between and within the fragments is marked in a grey scale. Another useful descriptor results from summing up the off-diagonal Ω_{AB}

values to obtain the so-called total charge transfer number (ω_{CT}). Its values go from zero to one, with $\omega_{CT} = 0$ indicating a pure LE state and $\omega_{CT} = 1$ a state with CT character.

For the inclusion of the crystal environment in the calculation of the exciton descriptors, we employ a hybrid quantum mechanics/molecular mechanics (QM/MM) approach with the electrostatic embedding scheme.[61] The pairs are included in the QM subsystem whereas the surrounding crystal environment is treated as point charges in the MM subsystem.

5.2. COMPUTATIONAL DETAILS

Calculation of electronic couplings. For the gas phase calculations, CASSCF(6,6)/ANO-S-VDZP molecular wave functions for the three tetracene molecules (highlighted in Figure 5.5) describing the ground state (S_0), the first excited state (S_1), the lowest triplet state (T_1), the cationic (D^+) and anionic (D^-) forms were generated with the OpenMolcas[62, 63] package. The geometries of the three tetracene molecules were taken directly from the crystal structure (CCDC code TETCEN). Please note that these geometries were used for the calculations of all the molecular states. In order to reduce the computational cost associated with the NOCI calculations, we have followed the protocol as explained in Ref. 64 to generate a reduced common molecular orbital (MO) basis for each of the three possible pairs. The common basis was generated with a program written in f95, and the molecular wave functions of the electronic states are now expressed in the new MO basis. For the three pairs, construction of the following six MEBFs: $\Phi_{S_0S_0}$, $\Phi_{S_0S_1}$, $\Phi_{S_1S_0}$, Φ_{1TT} , $\Phi_{D^+D^-}$ and $\Phi_{D^-D^+}$, and calculation of the Hamiltonian and overlap matrix elements are performed with the GronOR[45, 46] code. Finally, the electronic couplings are calculated as defined in eq. (5.3) between the localised excited states and the 1TT state. Two diabatic states, $\Phi_{S[1]}$ and $\Phi_{S[2]}$, were constructed from a 2×2 NOCI calculation in the basis of the $\Phi_{S_0S_1}$ and $\Phi_{S_1S_0}$ MEBFs, whereas the diabatic state of the coupled triplets corresponds to the Φ_{1TT} MEBF. Note that the S[1] and S[2] diabats are not necessarily the simple $+/-$ combinations of the S_0S_1 and S_1S_0 MEBFs as there is no inversion center between the pair of molecules. The importance of the charge transfer states in the description of the lower lying S[1], S[2] and 1TT states is explored by performing a 4×4 NOCI calculation with the $\Phi_{S_0S_1}$, $\Phi_{S_1S_0}$ and $\Phi_{D^+D^-}$, $\Phi_{D^-D^+}$ MEBFs on one hand, and a 3×3 NOCI with the Φ_{1TT} and $\Phi_{D^+D^-}$, $\Phi_{D^-D^+}$ MEBFs on the other. For the embedded cluster calculations, the frozen HF density for each molecule was generated considering twelve surrounding tetracene molecules with the ANO-S-MB basis set.

Excited state analysis. Excited state calculations were performed on the three tetracene pairs in the gas phase using TD-DFT within the Tamm-Dancoff approximation at the CAM-B3LYP/ANO-S-VDZP level of theory. The excited state calculations were carried out as implemented in the Q-Chem 5.3[65] quantum chemistry package. For the QM/MM calculations, each tetracene pair was included in the QM subsystem and treated at the same level of theory as in the gas phase. The MM region considered 123 molecules in a symmetrical portion of the crystal. The surrounding molecules were treated as Charge Model 5 point charges[66] as shown in Figure 5.4. Post-processing of results and generation of the *electron-hole* correlation plots were performed with the TheoDORE 2.2[67, 68] analysis package. In this contribution, we use a gray scale ranging from black (highest

Ω_{AB} value) to white (lowest Ω_{AB}) color. For the fragmentation scheme, we considered each molecule as an individual fragment which resulted in 2x2 *electron-hole* correlation plots in the case of dimers and in 3x3 plots for the trimers. For the QM/MM calculations of DPBF, four different QM regions were considered as explained in the next section. For the dimers the MM region included 178 molecules and 177 for the trimers.

Figure 5.4 | Point charge values used for the QM/MM calculations for tetracene (top) and DPBF (bottom). Due to symmetry, only equivalent charges are shown.

5.3. RESULTS AND DISCUSSION

Tetracene. Figure 5.5 highlights the three pairs considered for the QM calculations (AB, AC and BC) within the crystal structure.

Charge transfer mediated electronic couplings calculated for the three tetracene pairs, with and without considering the environment, are reported in Table 5.1. In the AC and BC pairs, the inclusion of the environment enhances V of the $S[1]$ state by 13 and 17 meV, respectively, and approximately 2 meV for $S[2]$ compared to the gas-phase values. The couplings are within the range of previously reported NOCI values for tetracene.[6, 47, 60] The parallel AB disposition shows the lower V value which translates to the lowest probability of SF to occur, while the highest probability is associated to the AC and BC pairs. Additionally, for the AB pair, the inclusion of the environment substantially enhances the coupling for S_1 while for S_2 remains unchanged. Our results suggest that the inclusion of the immediate adjacent molecules surrounding the pair does not change the electronic coupling qualitatively, indicating that the AC and BC pairs still exhibit larger V values than the AB pair.

Figure 5.5 | Crystal structure of tetracene. In the center, the three tetracene molecules included in the QM region are highlighted, and in grey the molecules considered in the MM region.

Table 5.1 | Charged transfer-mediated electronic couplings (in meV) of the photoexcited states with the 1TT state in the three tetracene pairs. Charge transfer states were allowed to mix with both states. S[1] and S[2] represent the diabatic states constructed in the basis of the S_0S_1 and S_1S_0 MEBFs.

Pair	Gas phase		Embedded cluster	
	$V_{S[1]}$	$V_{S[2]}$	$V_{S[1]}$	$V_{S[2]}$
AB	3.3	3.7	0.9	3.6
AC	41.8	14.8	54.2	17.6
BC	23.9	11.3	40.5	13.6

Table 5.2 compares the calculated exciton descriptors for the three tetracene pairs in the gas phase and with the QM/MM approach. The distance between the centers of mass of the molecules are also shown for each pair. As explained in section 5.1.2, the exciton descriptors can be used to assign the character of the excited states of the pairs.

For the AB pair in the gas phase model, S_1 is predicted as the brightest state. The value of $d_{h \rightarrow e}$ is zero for all four states, which suggest a LE character. Nevertheless, d_{exc} reveals that the character of the S_1 and S_2 states is different from S_3 and S_4 . The ω_{CT} values give more information about the real character of the excited states. For S_1 and S_2 , $\omega_{CT} \approx 0$ points at a ER character which is further supported by the positive values of R_{eh} revealing the states as highly correlated bound excitons. In the case of the next two states, $\omega_{CT} \approx 1$ would suggest a CT character but the negative values of R_{eh} clarifies that they actually correspond to CR states. Interestingly, we observed that in this pair the excitation energies of the two CR states are higher than the LE ones by 0.40 eV. A recent work on pentacene clusters studied the dependency of the relative CT state energies with respect to different functionals and cluster size. The results indicate that low-lying CT states

Table 5.2 | Exciton descriptors of the four lowest singlet excited states of the tetracene pairs calculated at the CAM-B3LYP/ANO-S-VDZP level of theory in the gas phase and with a QM/MM approach employing an electrostatic embedding scheme. Excitonic resonance (ER), charge resonance (CR), locally excited (LE) and charge transfer (CT) states are assigned for each of the states. Distance between the centers of mass of the molecules is reported

Pair	Distance (Å)	System	State	$\Delta E(\text{eV})$	f	ω_{CT}	$d_{exc}(\text{Å})$	$d_{h \rightarrow e}(\text{Å})$	R_{eh}	Character
AB	6.35	Gas phase	S_1	3.06	0.406	0.01	4.689	0.000	0.458	ER
			S_2	3.06	0.000	0.02	4.731	0.000	0.459	ER
			S_3	3.46	0.002	0.97	7.353	0.000	-0.374	CR
			S_4	3.47	0.000	0.98	7.377	0.000	-0.385	CR
		QM/MM	S_1	3.05	0.402	0.01	4.684	0.011	0.457	ER
			S_2	3.05	0.001	0.02	4.727	0.004	0.458	ER
			S_3	3.45	0.001	0.97	7.366	5.537	0.017	CT
			S_4	3.47	0.000	0.98	7.368	5.537	0.015	CT
AC	5.20	Gas phase	S_1	2.84	0.037	0.83	6.352	3.995	0.052	CT
			S_2	2.92	0.094	0.04	4.662	0.123	0.084	LE
			S_3	3.10	0.169	0.16	5.014	0.683	0.096	LE
			S_4	3.55	0.003	0.78	6.222	3.752	0.063	CT
		QM/MM	S_1	2.90	0.085	0.06	4.734	0.249	0.105	LE
			S_2	2.97	0.123	0.44	5.621	2.069	0.084	LE
			S_3	3.16	0.085	0.54	5.820	2.591	0.068	CT
			S_4	3.35	0.008	0.92	6.512	4.439	0.044	CT
BC	5.50	Gas phase	S_1	2.80	0.076	0.69	6.024	3.221	0.055	CT
			S_2	2.97	0.059	0.16	4.951	0.701	0.215	LE
			S_3	3.07	0.178	0.20	5.082	0.488	0.111	LE
			S_4	3.55	0.011	0.87	6.310	4.077	0.057	CT
		QM/MM	S_1	2.88	0.160	0.21	5.066	0.655	0.068	LE
			S_2	3.00	0.083	0.14	4.940	0.256	0.185	LE
			S_3	3.14	0.045	0.81	6.228	2.742	-0.067	CT
			S_4	3.34	0.035	0.84	6.277	3.694	0.015	CT

become accessible at larger cluster sizes, and these are predicted by optimally-tuned functionals but not by common hybrid ones. The work encourages further studies beyond the dimer model.[32] The QM/MM exciton descriptors for the first two states of the AB pair (S_1 and S_2) reveal that they remain ER states as in the gas phase model. Nevertheless, the character of the S_3 and S_4 states has changed, and are now better described as CT states. This assignment is beyond doubt as it is based on the combination of the non-zero values of $d_{exc} = 5.537$ Å and the low positive values of R_{eh} of approximately 0.016. Even though the character changed, the CT states remain higher in energy than the ER ones. In both the gas phase and QM/MM framework, the S_1 and S_2 states turn out to be degenerate (3.06 eV in gas phase and 3.05 eV in QM/MM) as well as S_3 and S_4 (≈ 3.465 eV in gas phase and ≈ 3.46 eV in QM/MM) which is a consequence of the symmetric parallel relative orientation of the molecules in the AB pair. Please note that the AB dimer possesses an inversion center whereas AC and BC do not. Our results put in evidence that the inclusion of the environment has a large effect on the exciton descriptors of this pair, and subsequently in the character of the excited states. We speculate that in this disposition SF is not favoured due to the formation of pure ER states without any CT-mixing.

The excited-state character and order in the pairs AC and BC are similar, both in gas phase and QM/MM framework. The recognition of the state character is less straightfor-

ward than in the AB pair but, even then, the exciton descriptors facilitate their assignment. In the gas phase, S_1 and S_4 can be assigned as pure separated CT states since $d_{h \rightarrow e} > 3.2 \text{ \AA}$ and $\omega_{CT} > 0.69$. Based on the same descriptors, S_2 and S_3 are identified as LE since their $d_{h \rightarrow e}$ are less than $1 \text{ \AA}$ and the ω_{CT} values are closer to zero. Nevertheless, the fact that these descriptors are non-zero hints to a non-negligible CT contribution to the character of both LE states. Less obvious indications on the different state character are given in the d_{exc} where for the CT states the values are higher than $6 \text{ \AA}$. Unlike the AB pair, the CT and LE states are now closer in energy. Although the inclusion of the environment does not change the character of the four states since two CT and two LE are still identified, the state order is affected by the electrostatic embedding. In this sense that the two lowest singlet states obtained using the QM/MM approach have LE character with small CT contribution while S_3 and S_4 correspond to the CT states. Despite this new state order, LE and CT characters are observed for these two pairs in contrast with the ER observed in the AB pair.

The *electron-hole* correlation plots of the tetracene pairs are shown in Figure 5.6. These plots provide an insight beyond the descriptors on where the excitons might be located and from where the CT occurs within the chosen fragmentation scheme. Please note that we consider each molecule as an individual fragment. For the pair AB, it is confirmed that S_1 and S_2 correspond to ER states whereas S_3 and S_4 correspond to CR states. Interestingly, no grey off-diagonal contributions are predicted in the plots of the ER states which indicates no CT contribution. The pattern in the correlation plots change for the AB pair when the environment is included in the description. The QM/MM correlation plots (second row in Figure 5.6) corroborates that the S_1 and S_2 states remain with ER character as in the gas phase. Nevertheless, S_3 and S_4 are now predicted as CT states while in the gas phase they were initially identified as CR states. These changes highlight how the inclusion of the environment influences the character of the higher excited states as further confirmed by the character assignments discussed based on the exciton descriptors reported in Table 5.2.

The gas phase correlation plots of the AC pair (third row in Figure 5.6), further confirm that that S_1 and S_4 correspond to CT states. The LE character of S_2 and S_3 is also corroborated by the corresponding plots with the excitons located in molecules C and A, respectively. The QM/MM plots for this pair (fourth row in Figure 5.6) show the influence that the environment has on the state order and character. We observe that the S_2 and S_3 states in the QM/MM approach resemble linear combinations of the S_1 and S_3 states in the gas phase. S_1 now corresponds to a LE state with the exciton localised in molecule C. S_2 (one of the linear combinations) has also LE character with the exciton now localised in molecule A. It is worth to note a pronounced off-diagonal element in the QM/MM plot of S_2 (second plot in fourth row of Figure 5.6) which suggests a higher CT contribution than the similar LE state (third plot in third row of Figure 5.6) in the gas phase. S_3 and S_4 are now the CT states, with S_3 (the second of the linear combinations) having a notable LE contribution to its character. For the AC dimer, we have computed the excited state character and their relative ordering under the conductor-like polarizable continuum model[69] (C-PCM) approach employing three different values of the dielectric constant (3, 5 and 40) as shown in Figure 5.13 and Table 5.7. The state character and order in the C-PCM analysis is similar to that obtained with the electrostatic embedding in the

Figure 5.6 | *Electron-hole correlation plots of the three tetracene pair arrangements within the crystal structure in the gas phase and with the QM/MM approach. Pairs were treated at the CAM-B3LYP/ANO-S-VDZP level of theory in the QM region, while the rest of the crystal structure was included in the MM region as electrostatic embedding.*

QM/MM approach.

A similar analysis can be done for the BC pair. In the gas phase plots (fifth row of Figure 5.6), S_1 and S_4 have CT character whereas S_2 and S_3 correspond to the LE states with the excitons localised in molecules C and B, respectively. When the environment is switched on, the resulting QM/MM plots (last row in Figure 5.6) show that the state order and character has changed compared to the corresponding plots in the gas phase. S_1 and S_2 correspond to LE states with exciton being localized on molecule C and B, respectively. S_3 and S_4 can be easily assigned to CT states based on the correlation plots. The character of the states in the three dimers for both the gas phase and the QM/MM environment is further validated with the corresponding MEBFs coefficients of each state as shown in Tables 5.8-5.13 of the Appendix.

The QM/MM results show how the nature of the excited states change with both (i) the orientation of the molecules in the pairs and (ii) when the environment is taken into account. Despite these changes, the underlying mechanism remains similar for both the gas phase and the QM/MM approach. We observed that the LE states are mixed with CT character for the pairs with $V \gg 0$, which highlights that this mixing is responsible for the enhancement of the electronic coupling. Both, the electronic couplings and exciton descriptors, when including the environment, point to a CT-mediated superexchange mechanism, as in our previously reported work.[60]

DPBF. Panel (a) of Figure 5.7 shows the long-range packing of the two known polymorphs of DPBF referred to as α and β forms. Experimental measurements on polycrystalline thin films of both polymorphs revealed that the α form exhibits SF with different yields depending on the temperature, whereas fluorescence predominates in the β form quenching the formation of the 1TT state.[70] Both polymorphs have almost an identical crystal structure: They consist of slipped-stacked and herringbone pairs and the possible nearest-neighbour pairs[25] are practically the same in both forms. The only difference between the two forms lies in the next-nearest neighbour interactions.[25] For clarity, a superposition of a portion of the α and β polymorphs is shown in panel (b) of Figure 5.7. Here, it is clear that the nearest-neighbour pairs formed between the molecules in rows I and II are similar for both polymorphs. The major difference appears when a next-nearest neighbour molecule (from row III) is considered into the description. This stresses that a gas-phase dimer model would not be enough to explain the difference in SF efficiency between the two, and that the inclusion of the crystal environment is essential. Here, we apply the exciton descriptors to unravel differences in the excited states in both polymorphs where each DPBF molecule is considered as an individual fragment.

We have considered six different QM regions of DPBF (for the gas phase and the QM/MM calculations) which were identified within and between the stacks of the polymorphs (see Figure 5.8). Two of them correspond to dimers found within the stack and a superposition of these is depicted in panel (a) of Figure 5.9. As can be seen, the dimers are almost identical for both polymorphs. One can define another two additional dimer arrangements between the stacks formed by molecules in row I and II. The superposition (panel (b) of Figure 5.9) puts in evidence that they are also nearly identical. The other two QM regions consist of trimer arrangements that include one nearest and one next-nearest neighbours between stacks for both polymorphs. It is clear from the superposition, shown in panel (c) of Figure 5.9, that the differences between the polymorphs in the next-nearest neighbour molecules (molecule III).

Figure 5.7 | The two polymorphs of DPBE a) The long-range packing of the α and β forms are depicted. Vector lengths are indicated in each polymorph. b) Superposition of a portion of the α (blue) and β (red) polymorphs. Nearest-neighbours are almost identical (rows I and II) whereas next-nearest are different (row III).

Figure 5.8 | Depiction of the a) dimer identified within the stack, and b) the trimer arrangement formed between stacks in the crystal structure of the α polymorph of DPBE.

Table 5.3 collects the charged-mediated electronic couplings for the dimer and trimers formed for molecules I, II and III in the α and β polymorphs. A NOCI calculation on a

Figure 5.9 | The QM regions of DPBF treated in this contribution. a) Dimer arrangements identified within the stack; d) dimers identified between the stacks and c) trimer arrangements between different stacks of the α (blue) and β (red) polymorphs.

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trimer is not yet feasible with the current implementation. For this case, the Hamiltonian and overlap matrix elements were obtained employing the *ab initio* Frenkel-Davydov excitation model[37, 71–74] (AIFDEM) which is in principle a similar methodology to NOCI. In a previous comparison for dimers in the gas phase, we have established that the couplings calculated with the NOCI and AIFDEM methodologies have a qualitative agreement.[6] The AIFDEM calculations reveal that the dimers in both polymorphs have similar couplings in the gas phase (0.7 meV), which is not unexpected because of the almost identical conformation of both dimers. Inclusion of environment leads to a larger enhancing in α than in β . A similar trend is observed for the trimers, where the couplings are enhanced within the QM/MM approach in comparison with their gas phase counterparts. Larger values are (> 21.2 meV) calculated for α which implies that SF occurs faster than in β where the couplings are < 8.9 meV. A previous study has suggested that besides electronic factors, such as energies and couplings, entropic contributions might play an important role in the solids to explain differences in SF yields.[75]

Table 5.4 collects the exciton descriptors calculated for the dimer parallel arrangements within the stack (panel (a) in Figure 5.9) of the α and β forms in the gas phase and the QM/MM description. As expected, the exciton descriptors of the four states calculated in the gas phase are similar for both dimers taken from both polymorphs since they are almost identical. This leads to identical state character and order. Exciton descriptors for S_1 and S_2 states suggest in principle LE character since the $d_{h \rightarrow e}$ and ω_{CT} are almost zero and the larger R_{eh} values of approximately 0.47. Nevertheless, the *electron-hole* correlation plots in Figure 5.10 unravel that they correspond to ER states since the exciton is predicted to be delocalised over the two molecules. S_2 is predicted as the bright state. For S_3 and S_4 , $\omega_{CT} \approx 1$ and the negative signs of R_{eh} point to a CR character which is also confirmed by the corresponding *electron-hole* correlation plots. Interestingly, the $d_{h \rightarrow e}$ values calculated for the CR states (S_3 and S_4) in the dimer from β in the gas phase are lower than those in the dimer from α by 0.2 Å. This points to a lesser CT contribution to the character of the states in the β polymorph.

The QM/MM results for the dimer from the β polymorph show that the order of the states and their character are similar to their correspondence in the gas phase with S_1 and S_2 identified as ER states and S_3 and S_4 as CR ones. These assignments are based

Table 5.3 | Charged-mediated electronic couplings (in meV) of the photoexcited states with the 1TT states in the dimers and trimers of DPBF. Charge transfer states were allowed to mix with both states. Subscript X in $\Phi_{S[X]}$ indicates for the photoexcited states where the exciton is located, and X,Y in $\Phi_{TT[X,Y]}$ represents in which monomers the triplets are placed.

Polymorph	System		$\Phi_{S[I]}$	$\Phi_{S[II]}$	$\Phi_{S[III]}$
α	Dimer I-II	$\Phi_{TT[I,II]}$	Gas phase	0.7	0.6
			QM/MM	19.7	28.3
	Trimer	$\Phi_{TT[I,II]}$	Gas phase	3.7	1.6
			QM/MM	21.2	28.1
		$\Phi_{TT[II,III]}$	Gas phase	0	1.9
			QM/MM	0	28.3
β	Dimer I-II	$\Phi_{TT[I,II]}$	Gas phase	0.7	0.7
			QM/MM	4.1	2.9
	Trimer	$\Phi_{TT[I,II]}$	Gas phase	0.7	0.4
			QM/MM	8.9	2.7
		$\Phi_{TT[II,III]}$	Gas phase	0	0.1
			QM/MM	0	0.1

Table 5.4 | Exciton descriptors calculated at the CAM-B3LYP/ANO-S-VDZP for the identified DPBF dimers within the stack in the α and β polymorphs in the gas phase and with electrostatic embedding (QM/MM approach).

Polymorph	System	State	$\Delta E(\text{eV})$	f	ω_{CT}	$d_{exc}(\text{\AA})$	$d_{h \rightarrow e}(\text{\AA})$	R_{eh}	Character
α	Gas phase	S_1	3.419	0.000	0.010	4.201	0.518	0.487	ER
		S_2	3.489	1.234	0.046	4.280	0.605	0.475	ER
		S_3	3.893	0.000	0.978	6.671	0.624	-0.372	CR
		S_4	3.909	0.025	0.947	6.609	0.629	-0.339	CR
	QM/MM	S_1	3.391	0.030	0.040	4.282	0.614	0.443	LE
		S_2	3.445	0.938	0.205	4.741	1.078	0.313	LE
		S_3	3.578	0.236	0.766	6.163	3.862	0.070	CT
		S_4	4.207	0.001	0.954	6.688	4.986	0.022	CT
β	Gas phase	S_1	3.446	0.000	0.010	4.184	0.512	0.488	ER
		S_2	3.515	1.230	0.044	4.258	0.599	0.477	ER
		S_3	3.925	0.000	0.978	6.659	0.435	-0.376	CR
		S_4	3.940	0.023	0.948	6.599	0.442	-0.344	CR
	QM/MM	S_1	3.446	0.000	0.010	4.184	0.512	0.488	ER
		S_2	3.515	1.230	0.044	4.258	0.599	0.477	ER
		S_3	3.925	0.000	0.978	6.659	0.421	-0.377	CR
		S_4	3.940	0.023	0.948	6.600	0.428	-0.344	CR

on both the exciton descriptors and the *electron-hole* correlation plots at the bottom of Figure 5.10. The similar values on the exciton descriptors and the identical correlation plots suggest that the character of the states in the dimer within the stacks of the β form is not affected when the environment is taken into consideration.

In contrast to the results for β , the character of the states in the dimer from α is highly affected under the presence of the environment within the QM/MM framework. The S_1 and S_2 states have now LE character with CT contribution inferred by the gray off-diagonal elements and the non-zero values of the $d_{h \rightarrow e}$ and ω_{CT} exciton descriptors. This is contrary to the gas-phase results where S_1 and S_2 are identified as ER states.

Additionally, the characters of S_3 and S_4 are affected as well; they were identified as CR states in the gas phase, while within the QM/MM approach they correspond to CT states, easily assigned by the large $d_{h \rightarrow e}$ of 3.862 Å (for S_3) and 4.986 Å (for S_4) and their ω_{CT} values close to one (0.766 and 0.954). The QM/MM R_{eh} values of 0.070 and 0.022 (S_3 and S_4 , respectively) for the CT states suggest that the hole and electron are loosely correlated but bound by the Coulombic force. This is again contrary to the gas phase results where the electron and hole are expected to avoid each other ($R_{eh} = -0.372$ and -0.339). The different character of the states in the dimer from α becomes clearer when one looks at the correlation plots in Figure 5.10. The QM/MM plots confirm that S_1 and S_2 correspond to LE states (excitons being localized on I.a and I.b, respectively) with CT contributions, and also show the CT character of the S_3 and S_4 states. This is in contrast with the resonance states predicted in the gas phase plots.

Figure 5.10 | Electron-hole correlation plots of the DPBF dimers identified within the stacks in the two polymorphs in the gas phase and with the QM/MM approach.

Our results reveal that considering the dimer model in the gas phase is not adequate to explain the experimentally observed difference in SF yields of the polymorphs, and

clear differences between the dimers are observed when the environment is switched on.

In sum, our results highlight that character of excited states in the dimer from α is highly affected by the inclusion of the environment compared to the dimer from β . We observe the presence of LE and CT states in α , which exhibits SE, whereas resonance states are observed in β . Results for the slipped-stack pairs are not enough to explain the difference in SF efficiency. In fact, a previous study has shown that the largest calculated excitonic couplings and SF matrix elements occurs between molecules that are not collocated within the slipped stacks. This conclusion indicates the study should be focused primarily in molecules between different stacks and not within the stack[70] (see Figure 5.8). Despite this conclusion, the QM/MM exciton descriptors put in evidence differences between the polymorphs for the similar dimers when the environment is considered. We observe a localisation of excitons within the slipped stacks in the α form which is in line with experimental evidence of the delocalisation not being great in either polymorph.[39] We speculate that these local excitons could undergo SF more efficiently with neighboring stack molecules than the ER states formed in the β form.

The exciton descriptors for the two dimers formed between stacks (panel (b) in Figure 5.9) are presented in Table 5.5. As expected the state character and order in the gas phase for both dimers from the polymorphs is identical. S_1 and S_2 are assigned as LE states while S_4 and S_5 are CT ones. The character is further confirmed by the corresponding *electron-hole* correlation plots depicted in the first and third row of Figure 5.11. The nearly identical values of the exciton descriptors for the four states, as well as the similar correlation plots, confirms that the states are practically the same in the gas phase for both dimers. Please note that the the largest difference between this interstack dimers and the previously discussed intrastack dimers is the relative orientation of the two molecules, which reflects already how this affects, at first, the character of the excited states.

Changes are observed when the environment is taken into consideration although they are less pronounced. For these two dimers, we observed a localisation of the excitons in the S_1 and S_2 states in the QM/MM plots (first and third rows in Figure 5.11) whereas S_3 and S_4 remain as CT states but the order has exchanged compared with the gas phase results. Similar QM/MM results for the dimers suggest that inclusion of the environment within the electrostatic embedding scheme is not able to capture totally the effect that the next-nearest molecules has on excited states (in row III) and that inclusion of an explicit third molecule in the QM regions might capture further effects.

Table 5.6 reports the exciton descriptors calculated for the trimer arrangements. For both trimers in the gas phase, the first three lowest states (S_1 , S_2 and S_3) are identified as LE with minor CT contributions. This assignment is done based on the zero values of ω_{CT} and $d_{h \rightarrow e} < 0.6 \text{ \AA}$. Comparing the descriptors of these three states in the gas phase for both polymorphs, we observe that the d_{exc} and $d_{h \rightarrow e}$ values are almost identical. Nevertheless, the corresponding R_{eh} values indicate that the LE character of the S_1 (0.721 for α and 0.836 for β) and S_2 (0.918 for α and 0.828 for β) states is different, whereas the descriptors for the S_3 are similar for both polymorphs. These differences point to bound excitons but with different degree of correlation and character. The *electron-hole* correlation plots shine light on these differences. If we compare the gas phase plots (first and third rows in Figure 5.12) we can identify them. In the case of S_1 , the exciton is predicted to be localised in molecule II in α whereas in the β form it would be localised predominantly in molecule

Table 5.5 | Exciton descriptors calculated at the CAM-B3LYP/ANO-S-VDZP for the identified DPBF dimers between stacks in the α and β polymorphs in the gas phase and with electrostatic embedding (QM/MM approach).

Polymorph	System	State	$\Delta E(\text{eV})$	f	ω_{CT}	$d_{exc}(\text{\AA})$	$d_{h\rightarrow e}(\text{\AA})$	R_{eh}	Character
α	Gas phase	S_1	3.491	0.687	0.001	4.175	0.588	0.726	LE
		S_2	3.496	0.717	0.000	4.174	0.584	0.726	LE
		S_3	4.536	0.000	1.000	10.840	9.875	-0.003	CT
		S_4	4.544	0.000	0.998	10.547	9.587	-0.002	CT
	QM/MM	S_1	3.447	0.647	0.001	4.175	0.832	0.219	LE
		S_2	3.466	0.670	0.000	4.174	0.752	0.219	LE
		S_3	4.399	0.000	0.999	10.384	9.423	-0.002	CT
		S_4	4.643	0.000	0.999	10.978	10.031	-0.003	CT
β	Gas phase	S_1	3.517	0.685	0.001	4.158	0.582	0.723	LE
		S_2	3.522	0.713	0.000	4.156	0.578	0.722	LE
		S_3	4.567	0.000	1.000	10.801	9.841	-0.003	CT
		S_4	4.574	0.000	0.998	10.519	9.565	-0.003	CT
	QM/MM	S_1	3.545	0.734	0.001	4.175	0.410	0.529	LE
		S_2	3.554	0.764	0.000	4.184	0.365	0.528	LE
		S_3	3.751	0.000	0.999	10.642	9.692	-0.003	CT
		S_4	4.662	0.061	0.000	4.557	1.711	0.090	LE

III (see Figure 5.9). The differences in the S_2 state are even more pronounced since the exciton in the trimer from α is predicted to be delocalised mainly between molecules I and III whereas in β it would correspond to a delocalised exciton predominantly in molecules I and II. The almost identical plots for S_3 (predicted as the brightest state since it has the larger f value) confirm that this state has similar character for both trimers in the gas phase, an exciton delocalised over the three molecules with the major contribution coming from molecule I.

The gas phase exciton descriptors for the S_4 , S_5 and S_6 states lead to a CT character in both polymorphs. The assignment can be safely done by the $\omega_{CT} \approx 1$ and the $d_{exc} > 9 \text{\AA}$. Interestingly, direct comparison of the exciton descriptors for each of these three states between both polymorphs suggests a similar character in both trimers since the values of the descriptors are almost identical. The *electron-hole* correlation plots (Figure 5.12) indicate from where to where the CT occurs. The gas phase plots for α (first row) show that in the S_4 state there is CT from molecule I to II. In the case of S_5 , the CT occurs from molecule III to II and in S_6 the transfer goes from molecule II to III. The gas phase correlation plots of S_4 , S_5 and S_6 of the trimer from β (third row) are almost identical to the ones in α which confirms that the character is the same for these states in both trimers of the polymorphs.

For both polymorphs, the QM/MM descriptors for the trimers show that the S_1 , S_2 and S_3 states have LE character, as in the gas phase results, since $\omega_{CT} = 0.0$ and the close-to-zero $d_{h\rightarrow e}$ values. It is worth to point out that the QM/MM $d_{h\rightarrow e}$ values of the states in the β form are lower than those in the α form, e.g., for S_1 , $R_{eh} = 0.829$ in α and 0.529 in β ; for S_2 , $R_{eh} = 0.836$ in α and 0.432 in β ; and for S_3 , $R_{eh} = 0.755$ in α and 0.398 in β . These changes are also reflected in the correlation plots in Figure 5.12. For the S_1 state, the correlation plot indicates that the exciton in the α form is delocalised between molecules II and III (first plot from the second row) whereas in the β form the exciton is

Figure 5.11 | *Electron-hole correlation plots of the DPBF dimers identified between the stacks in the two polymorphs in the gas phase and with the QM/MM approach.*

predominantly localised on molecule II (first plot in the fourth row). As in S_1 , the exciton formed in S_2 is also delocalised. In the trimer extracted from the β polymorph, there is a localised exciton on molecule III with a minor delocalisation onto molecule I (second plot in fourth row in Figure 5.12). This is contrast with S_2 calculated for the α polymorph, where the delocalisation is more pronounced particularly across molecules II and III (second plot in second row in Figure 5.12). For S_3 , the plots for both polymorphs are almost identical, suggesting a similar character with the exciton predominantly localised on molecule I with minor contributions from molecule III.

S_4 , S_5 and S_6 states are straightforwardly assigned as CT states from the QM/MM exciton descriptors in Table 5.6 in both polymorphs. The character follows immediately from $\omega_{CT} \approx 1$ and $d_{exc} > 9\text{\AA}$. It is important to note that the corresponding R_{eh} values of these states range from 0.000 to -0.003 for both polymorphs. These values suggest that the electron and hole generated after the CT are either not correlated. However, there is a major difference in the S_4 state for both polymorphs. $d_{h \rightarrow e}$ is 9.422 $\text{\AA}$ and 19.305 $\text{\AA}$ for

Table 5.6 | Exciton descriptors calculated at the CAM-B3LYP/ANO-S-VDZP for the identified DPBF trimers in the α and β polymorphs in the gas phase and with electrostatic embedding (QM/MM approach).

Polymorph	System	State	$\Delta E(\text{eV})$	f	ω_{CT}	$d_{exc}(\text{\AA})$	$d_{h \rightarrow e}(\text{\AA})$	R_{eh}	Character
α	Gas phase	S_1	3.489	0.778	0.000	4.176	0.588	0.721	LE
		S_2	3.491	0.051	0.000	4.175	0.583	0.918	LE
		S_3	3.498	1.257	0.000	4.174	0.590	0.903	LE
		S_4	4.527	0.000	0.998	10.553	9.593	-0.002	CT
		S_5	4.530	0.000	1.000	10.852	9.888	-0.003	CT
		S_6	4.548	0.000	0.998	10.545	9.584	-0.002	CT
	QM/MM	S_1	3.443	0.640	0.000	4.174	0.829	0.747	LE
		S_2	3.447	0.446	0.000	4.173	0.836	0.803	LE
		S_3	3.466	0.857	0.000	4.174	0.755	0.574	LE
		S_4	4.405	0.000	0.999	10.384	9.422	-0.002	CT
		S_5	4.497	0.000	0.998	10.360	9.394	-0.002	CT
		S_6	4.538	0.000	1.000	11.024	10.086	-0.003	CT
β	Gas phase	S_1	3.515	0.369	0.000	4.159	0.583	0.836	LE
		S_2	3.516	0.412	0.000	4.159	0.575	0.828	LE
		S_3	3.526	1.291	0.000	4.157	0.585	0.904	LE
		S_4	4.559	0.000	0.998	10.521	9.567	-0.003	CT
		S_5	4.562	0.000	1.000	10.810	9.851	-0.003	CT
		S_6	4.578	0.000	0.998	10.519	9.563	-0.002	CT
	QM/MM	S_1	3.529	0.719	0.000	4.169	0.529	0.332	LE
		S_2	3.540	0.176	0.000	4.175	0.432	0.867	LE
		S_3	3.553	1.288	0.000	4.181	0.398	0.859	LE
		S_4	3.776	0.000	1.000	19.807	19.305	0.000	CT
		S_5	3.925	0.000	0.999	10.604	9.647	-0.003	CT
		S_6	3.950	0.000	0.999	10.584	9.636	-0.003	CT

the α and β forms, respectively. This points to a larger separation in space of the charges in this particular state of the trimer from β . The $d_{h \rightarrow e}$ values for S_5 are similar for both polymorphs (9.394 and 9.647 Å) and slightly different for S_6 (10.086 and 9.636 Å).

The *electron-hole* correlation plots offer an insight on where the exciton might be located. For the S_4 state, the plots reveal that the CT in α occurs from molecule I to II (dark off-diagonal element in the fourth graph in the second row) whereas in the β form the CT occurs from molecule I to III (dark off-diagonal element in the fourth graph in the fourth row). This explains the difference in the distance between the charges in both polymorphs. The plots of the S_5 state are identical for α and β with the CT occurring from molecule II to III. For S_6 , the CT occurs from molecule III to II in the case of α and from molecule I to II in the β form.

We observe that, for both polymorphs, the QM/MM plots show a localisation of the excitons in the S_1 , S_2 and S_3 states in comparison with the gas phase, particularly in the β form. Experimental evidence suggest that in films of the β form loss of energy occurs due to presence of low energy states, such as excimers or traps.[70] Our QM/MM results hint to two main differences: (1) the exciton formed in S_3 (the brightest state) of the β form has a higher correlation ($R_{eh} = 0.859$) than the one in the brightest state (S_3) in the α polymorph ($R_{eh} = 0.574$). This high correlation suggests that the excitons formed are more tightly bound in the β form, and this might hinder the conversion to the 1TT state; and (2) the possible formation of CT states leads to larger separated electron and hole

Figure 5.12 | Electron-hole correlation plots of the DPBF trimers identified in the two polymorphs in the gas phase and with the QM/MM approach.

(≈ 19 Å) in the case of the β form which could function as a trap since the generated charges are not correlated ($R_{eh} \approx 0$) and might move freely through the crystal.

Comparison of the gas phase correlation plots of the dimers (first and third rows in Figure 5.11) and trimer (first and third rows in Figure 5.12) arrangements reveals that the changes are not particularly significant. The gas phase plots of the trimers (first and third rows of Figure 5.12) show that adding the third molecule in both trimers give slightly different state character for two of the LE states, i.e. S_1 and S_2 . The S_3 , S_4 , S_5 and S_6 states seem to be similar for both trimers. Differences are already discernible when we consider the QM/MM results. In the case of the trimer extracted from the α polymorph, inclusion of the environment results in excitons predominantly localised in one of the molecules, i.e., molecule II in S_1 , molecule III in S_2 and molecule I in S_3 (second row of Figure 5.12). As can be seen, the localisation in the QM/MM plots is less pronounced in α than in β for the above mentioned states. The environment seems to have a larger effect for the LE states in the trimer from the β polymorph than in the trimer from α .

In overall, the QM/MM exciton descriptors are able to spot differences between the two polymorphs (for the dimers and trimer arrangements considered) which highlights the importance of going beyond the gas-phase dimer model for certain chromophores and the potential of the excited state analysis to explore and unravel differences for other polymorphic systems. As for tetracene, the AIFDEM eigenvectors (Tables 5.14-5.25 of the Appendix) corroborate the character of the identified states employing TD-DFT in the gas phase and within the QM/MM approach in the dimers and trimers of DPBF.

5.4. CONCLUSIONS

To summarize, we have explored the influence of the crystal packing on the electronic couplings and the character of excited state of different molecular arrangements of tetracene and DPBF, two chromophores known to exhibit singlet fission.

Three tetracene pairs were identified within the crystal structure exhibiting different electronic coupling values. These couplings are enhanced when the environment is considered for two of these pairs (AC and BC), while in the parallel AB disposition this is not observed. The results indicate that, even though the numerical value changes, the inclusion of surrounding adjacent molecules do not change the electronic couplings qualitatively with AC and BC exhibiting larger values than AB. Gas phase exciton descriptors for the tetracene pairs revealed that the excited state character of the dimers is affected, in the first instance, by the mutual disposition of the molecules. On top of this, inclusion of the environment affects the excited state character and order of the dimers particularly on AB. Within the QM/MM framework, we observed LE and CT states in the pairs with non-zero electronic coupling (AC and BC), and ER and CT states in AB. Despite these differences, the electronic couplings and exciton descriptors show that the LE states mix with CT ones which points to a CT-mediated superexchange mechanism in both the gas phase and the QM/MM approach.

We illustrated how the excited state analysis can be used to unravel differences between two different polymorphs, namely α and β , which exhibit different SF yields with α showing the higher SF efficiency. First, we identified dimer arrangements within the stacks of the polymorphs. These dimer arrangements are almost identical in both the α and β forms. This leads to a similar excited state character and order in the gas phase. Differences in the excited states of the dimers are solely spotted when the crystal environment is taken into consideration. We observe ER and CR states in the β while in α LE and CT states are found. We speculate that these local excitons in α might undergo SF easier than the resonance states formed in the β polymorph.

We also studied the excited states in dimers and trimers formed between molecules in different stacks in the crystal structures of the polymorphs. The results for the trimers stress the effect that the relative orientation of the molecules has, at first, on the excited state character. We identified that, for the trimer arrangements in the α and β forms, the differences in the excited state character are more pronounced with the inclusion of the crystal packing within the QM/MM framework. Based on our QM/MM exciton descriptors, we speculate that the exciton formed in the brightest state of the β form is stronger correlated than the one formed in the brightest state in the trimer of α . We hypothesize that the formed excitons are more tightly bound in β than in α . This stronger interaction in the β polymorph could hinder the conversion of the photoexcited chromophore to the 1TT state explaining its lower SF efficiency. These observations emphasize that the inclusion of the environment is crucial to understand some of the experimental observations where the dimer model might not be adequate or enough.

5.5. APPENDIX

ANALYSIS OF THE AC TETRACENE DIMER WITH IMPLICIT ENVIRONMENT UNDER THE C-PCM APPROACH

Figure 5.13 | *Electron-hole* correlation plots of the four lowest singlet excited states of the AC tetracene dimer calculated at the CAM-B3LYP/ANO-S-DZV level of theory with implicit consideration of the environment using the conductor-like polarizable continuum model. Three different dielectric constant values were tested.

Table 5.7 | Exciton descriptors of the AC tetracene dimer calculated at the CAM-B3LYP/ANO-S-DZV level of theory with implicit consideration of the environment using the conductor-like polarizable continuum model. Different values of dielectric constant were tested.

Dielectric constant	State	$\Delta E(eV)$	f	ω_{CT}	$d_{exc}(\text{\AA})$	$d_{h \rightarrow e}(\text{\AA})$	R_{eh}
3	S_1	2.832	0.131	0.041	4.656	0.168	0.087
	S_2	2.905	0.193	0.310	5.343	1.446	0.087
	S_3	3.119	0.091	0.670	6.048	3.210	0.066
	S_4	3.382	0.007	0.932	6.546	4.528	0.045
5	S_1	2.830	0.132	0.046	4.668	0.191	0.083
	S_2	2.915	0.203	0.246	5.204	1.129	0.088
	S_3	3.146	0.078	0.733	6.166	3.516	0.063
	S_4	3.347	0.008	0.932	6.546	4.527	0.044
40	S_1	2.828	0.132	0.054	4.689	0.230	0.079
	S_2	2.924	0.224	0.182	5.064	0.817	0.089
	S_3	3.184	0.055	0.793	6.280	3.806	0.058
	S_4	3.301	0.011	0.927	6.535	4.498	0.043

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NOCI COEFFICIENTS FOR DIMER AB OF TETRACENE IN GAS PHASE

Table 5.8 | NOCI coefficients of the MEBFs for each of the states in the AB tetracene dimer in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0163879947	0.0326184562	-0.0017143516	0.0186147718	-0.0116895214
$\Psi_{S_0S_1}$	-0.6886361256	-0.6812479975	0.0051490887	0.1646688122	0.1844254748
$\Psi_{S_1S_0}$	0.6981237177	-0.6720588219	-0.0053941845	-0.1103149489	0.2209966565
$\Psi_{D_0^+D_0^-}$	-0.0183301187	0.0001893425	-0.0332884331	-0.7807105286	-0.5800879843
$\Psi_{D_0^-D_0^+}$	0.1287149044	-0.1923192327	0.0327418027	0.5959303929	-0.7684664354
Ψ_{1TT}	-0.1272566329	-0.1924907077	-0.9984300281	-0.0532340344	0.0076356900

NOCI COEFFICIENTS FOR DIMER AB OF TETRACENE WITHIN ENVIRONMENT

Table 5.9 | NOCI coefficients of the MEBFs for each of the states in the AB tetracene dimer within the embedded cluster approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0207713963	0.0015764954	-0.0000151766	0.0018742604	-0.0008645368
$\Psi_{S_0S_1}$	-0.7374600180	0.6745428844	0.0000488845	-0.0102349033	-0.0301137224
$\Psi_{S_1S_0}$	0.6743392994	0.7380078848	-0.0000308424	0.0210679303	-0.0043377444
$\Psi_{D_0^+D_0^-}$	0.0195308205	0.0069816432	0.0015979660	-0.9994027226	-0.0277567804
$\Psi_{D_0^-D_0^+}$	0.0165864516	-0.0207389411	-0.0008885431	0.0279185778	-0.9992637640
Ψ_{1TT}	-0.0000203579	0.0000579268	-0.9999968791	-0.0022977309	0.0012605533

NOCI COEFFICIENTS FOR DIMER AC OF TETRACENE IN GAS PHASE

5

Table 5.10 | NOCI coefficients of the MEBFs for each of the states in the AC tetracene dimer in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.1142570343	-0.1619990402	-0.0105682548	0.1773237073	-0.0326870036
$\Psi_{S_0S_1}$	0.9776315772	0.1925162022	0.0156587538	-0.0717921849	-0.0371242419
$\Psi_{S_1S_0}$	0.1127826315	0.7292796938	-0.0035909317	-0.4661727606	0.4881599628
$\Psi_{D_0^+D_0^-}$	-0.1344991129	0.6301805346	0.0065742959	0.8502714014	0.0541986962
$\Psi_{D_0^-D_0^+}$	-0.0155512693	0.0853111102	0.0044843290	0.1028896737	0.8775119150
Ψ_{1TT}	-0.0008624642	-0.0002790514	-1.0001993844	-0.0052073806	0.0022836208

NOCI COEFFICIENTS FOR DIMER AC OF TETRACENE WITHIN ENVIRONMENT

Table 5.11 | NOCI coefficients of the MEBFs for each of the states in the AC tetracene dimer within the embedded cluster approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.1214496443	0.2737342658	-0.0076988190	0.1626828163	-0.4028476716
$\Psi_{S_0S_1}$	-0.9700027448	-0.2242079872	-0.0118892816	-0.4632671256	0.0220587496
$\Psi_{S_1S_0}$	0.2227403069	-0.7697610529	-0.0105456983	0.8566024814	-0.3679058980
$\Psi_{D_0^+D_0^-}$	-0.0006317668	-0.5159896609	-0.0058505293	-0.1379450703	-0.8341319151
Ψ_{1TT}	0.0009090031	0.0045715229	0.9999060427	-0.0000951191	-0.0050949128

NOCI COEFFICIENTS FOR DIMER BC OF TETRACENE IN GAS PHASE

Table 5.12 | NOCI coefficients of the MEBFs for each of the states in the BC tetracene dimer in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0948382203	0.1144850107	0.0103434661	-0.0121419427	-0.0154864420
$\Psi_{S_0S_1}$	-0.7445303757	0.6672794993	0.0139278977	0.0108810358	0.0078507072
$\Psi_{S_1S_0}$	-0.6617600665	-0.7349053925	0.0147873633	-0.0023559670	-0.0192926440
$\Psi_{D_0^+D_0^-}$	0.0017872204	-0.0177822683	-0.0087268439	-0.9965219340	-0.0815798208
$\Psi_{D_0^-D_0^+}$	0.0044995716	0.0267001167	-0.0007002834	-0.0763797372	0.9969768806
Ψ_{1TT}	-0.0014904133	-0.0012590100	1.0003418214	0.0001167292	0.0002532096

NOCI COEFFICIENTS FOR DIMER BC OF TETRACENE WITHIN ENVIRONMENT

Table 5.13 | NOCI coefficients of the MEBFs for each of the states in the BC tetracene dimer within the embedded cluster approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0276858840	0.0008523775	0.0296876879	-0.0094299895	0.0396862053
$\Psi_{S_0S_1}$	0.9983813709	0.0026697629	-0.1241579979	-0.0119924253	0.1330118814
$\Psi_{S_1S_0}$	0.0056155406	-1.0221199346	0.1093015989	-0.0432489053	-0.5970448638
$\Psi_{D_0^+D_0^-}$	-0.0012001336	0.1270197565	-0.0799320488	-0.9984832904	-0.1597561767
$\Psi_{D_0^-D_0^+}$	0.0153592053	-0.0360086821	0.0595511914	-0.0173866486	-1.2070663758
Ψ_{1TT}	-0.0040124666	0.0050369378	1.0140154532	0.0004415150	0.0068675524

AIFDEM EIGENVECTORS IN THE EXCITON-SITE BASIS FOR THE I.A-I.B OF α IN THE GAS PHASE

Table 5.14 | AIFDEM coefficients of the MEBFs for each of the states in the I.a-I.b DPBF dimer of α in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0277737	0.0028854	-0.0007588	-0.0064482	0.0215616
$\Psi_{S_0S_1}$	-0.7324108	0.7077950	0.0034109	-0.0623480	0.0082529
$\Psi_{S_1S_0}$	0.7093863	0.7308431	-0.0033406	-0.0478294	-0.0395819
$\Psi_{D_0^+D_0^-}$	0.0278592	-0.0633481	-0.0290414	-0.8722924	0.4831785
$\Psi_{D_0^-D_0^+}$	0.0250671	0.0636147	-0.0289742	0.4811448	0.8734818
Ψ_{1TT}	0.0064934	0.0000345	1.0940155	-0.0108550	0.0374750

AIFDEM EIGENVECTORS IN THE EXCITON-SITE BASIS FOR THE I.A-I.B IN α WITHIN ENVIRONMENT

Table 5.15 | NOCI coefficients of the MEBFs for each of the states in the I.a-I.b DPBF dimer of α within the QM/MM approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.0000191	-0.0000144	-0.0000009	-0.0000191	-0.0000144
$\Psi_{S_0S_1}$	-0.9997001	0.0018118	-0.0246769	0.0000350	-0.0000133
$\Psi_{S_1S_0}$	0.0008422	0.9992429	0.0389297	-0.0000129	0.0000294
$\Psi_{D_0^+D_0^-}$	0.0000350	-0.0000133	0.0000003	-0.9997001	0.0018118
$\Psi_{D_0^-D_0^+}$	-0.0000129	0.0000294	0.0000007	0.0008422	0.9992429
Ψ_{1TT}	-0.0223357	-0.0394457	1.0929689	-0.0223357	-0.0394457

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AIFDEM EIGENVECTORS IN THE EXCITON-SITE BASIS FOR THE I.A-I.B IN β IN GAS PHASE

Table 5.16 | AIFDEM coefficients of the MEBFs for each of the states in the I.a-I.b DPBF dimer of β in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.0418105	0.0086049	-0.0008397	0.0054538	0.0205476
$\Psi_{S_0S_1}$	0.7382234	0.7010222	0.0034165	-0.0491583	0.0436482
$\Psi_{S_1S_0}$	-0.7021828	0.7365430	-0.0035112	-0.0666754	-0.008790
$\Psi_{D_0^+D_0^-}$	-0.0299693	-0.0653714	-0.0296590	-0.4611530	0.8839012
$\Psi_{D_0^-D_0^+}$	-0.0279021	0.0680036	-0.0292485	0.8825973	0.4634259
Ψ_{1TT}	-0.0067833	0.0002505	1.0924029	0.0115278	0.0379143

AIFDEM EIGENVECTORS IN THE EXCITON-SITE BASIS FOR THE I.A-I.B IN β WITHIN ENVIRONMENT

Table 5.17 | NOCI coefficients of the MEBFs for each of the states in the I.a-I.b DPBF dimer of β within the QM/MM approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.0167263	0.0164963	-0.0007205	0.0050219	0.0219513
$\Psi_{S_0S_1}$	0.7347262	0.7052121	0.0029714	-0.0497610	0.0411570
$\Psi_{S_1S_0}$	-0.7070430	0.7324009	-0.0032869	-0.0662809	-0.0074880
$\Psi_{D_0^+D_0^-}$	-0.0278757	-0.0648880	-0.0296331	-0.4592395	0.8849997
$\Psi_{D_0^-D_0^+}$	-0.0266463	0.0683569	-0.0292400	0.8835906	0.4615508
Ψ_{1TT}	-0.0061651	0.0004055	1.0924061	0.0116089	0.0378994

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AIFDEM EIGENVECTORS IN THE EXCITON-SITE BASIS FOR THE I-II IN α IN THE GAS PHASE

Table 5.18 | AIFDEM coefficients of the MEBFs for each of the states in the I-II DPBF dimer of α in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.0039296	-0.002	-0.0000002	-0.0000617	0.0003244
$\Psi_{S_0S_1}$	0.5240654	0.8757561	0.0000178	0.0010823	-0.0021444
$\Psi_{S_1S_0}$	0.8757588	-0.5240718	-0.0000449	-0.0021920	0.0011817
$\Psi_{D_0^+D_0^-}$	0.0000893	0.0024594	-0.0002189	-0.0000362	0.9999969
$\Psi_{D_0^-D_0^+}$	0.0013220	-0.0020684	0.0038038	0.9999898	0.0000421
Ψ_{1TT}	0.0000263	-0.0000323	1.0947486	-0.0040753	0.0002446

AIFDEM EIGEVectors IN THE EXCITON-SITE BASIS FOR THE I-II IN α WITHIN ENVIRONMENT

Table 5.19 | NOCI coefficients of the MEBFs for each of the states in the I-II DPBF dimer of α within the QM/MM approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Φ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	-0.0000381	-0.0000144	-0.0000009	-0.0000001	-0.0000001
$\Psi_{S_0S_1}$	0.0008422	0.9992429	-0.0246769	-0.0000002	-0.0000003
$\Psi_{S_1S_0}$	-0.99950021	0.0008221	0.0389297	0.0000001	-0.0000002
$\Psi_{D_0^+D_0^-}$	0.0000350	-0.0000133	0.0000003	0.0000001	0.9999987
$\Psi_{D_0^-D_0^+}$	-0.0000129	0.0000294	0.0000007	0.9999991	-0.0000002
Ψ_{1TT}	-0.0223357	-0.0394457	1.0929689	-0.0001920	-0.0019023

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AIFDEM EIGEVectors IN THE EXCITON-SITE BASIS FOR THE I-II IN β IN THE GAS PHASE

Table 5.20 | AIFDEM coefficients of the MEBFs for each of the states in the I-II DPBF dimer of β in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0258270	0.0092295	0.0000018	0.0001313	0.0003338
$\Psi_{S_0S_1}$	0.7974221	0.6361385	0.0000625	0.0024779	0.0013158
$\Psi_{S_1S_0}$	-0.6361485	0.7978020	0.0000293	0.0012771	0.0025338
$\Psi_{D_0^+D_0^-}$	-0.0011368	-0.0025518	0.0044709	0.9999861	-0.0000535
$\Psi_{D_0^-D_0^+}$	-0.0005439	0.0028084	-0.0003806	-0.0000452	-0.9999958
Ψ_{1TT}	-0.0000277	-0.0000532	1.0931556	-0.0047956	-0.0004188

AIFDEM EIGENVECTORS IN THE EXCITON-SITE BASIS FOR THE I-II IN β WITHIN ENVIRONMENT

Table 5.21 | NOCI coefficients of the MEBFs for each of the states in the I-II DPBF dimer of β within the QM/MM approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	Ψ_{1TT}	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$
$\Psi_{S_0S_0}$	0.0000047	-0.0000107	-0.0000000	-0.0000003	-0.0000000
$\Psi_{S_0S_1}$	1.0206298	0.0000314	-0.0000000	-0.0000002	-0.0000002
$\Psi_{S_1S_0}$	-0.0000315	1.0206264	-0.0000000	-0.0000002	-0.0000002
$\Psi_{D_0^+D_0^-}$	-0.0000290	-0.0000496	0.0012316	0.0000001	0.9999992
$\Psi_{D_0^-D_0^+}$	-0.0000348	1.0000000	0.000218	1.0000000	-0.0000003
Ψ_{1TT}	-0.0000000	-0.0002087	1.0934487	-0.0002087	-0.0014092

AIFDEM EIGEVECTORS IN THE EXCITON-SITE BASIS FOR THE TRIMER IN α IN GAS PHASE

Table 5.22 | AIFDEM coefficients of the MEBFs for each of the states in the DPBF trimer of α in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Psi_{S[3]}$	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$	$\Phi_{CT[3]}$
$\Psi_{S_0S_0S_0}$	-0.0038108	0.0025470	-0.0022037	0.0000000	0.0000042	-0.0000951
$\Psi_{S_1S_0S_0}$	0.3325867	-0.6800892	-0.6844498	0.0000000	-0.0000000	0.0000000
$\Psi_{S_0S_1S_0}$	0.6875237	0.6742966	-0.3358551	-0.0000000	-0.0000478	0.0000282
$\Psi_{S_0S_0S_1}$	0.6764227	-0.3519160	0.6783672	0.0000000	0.0000347	-0.0000531
$\Psi_{D_0^+D_0^-S_0}$	-0.0000006	0.0000034	0.0000013	0.0000000	0.0000000	-0.0000414
$\Psi_{D_0^+S_0D_0^-}$	-0.0000856	-0.0009760	-0.0020886	-0.0000499	-0.0000000	-0.0000000
$\Psi_{D_0^-D_0^+S_0}$	-0.0000032	-0.0000035	-0.0000006	1.0000000	-0.0000499	0.0000000
$\Psi_{S_0D_0^+D_0^-}$	0.0007365	0.0018191	-0.0014328	0.0000000	1.0000000	-0.0000000
$\Psi_{D_0^-S_0D_0^+}$	0.0011920	-0.0000069	0.0023457	-0.0000000	0.0000000	0.0000000
$\Psi_{S_0D_0^-D_0^+}$	0.0006568	-0.0015543	0.0018149	-0.0000414	-0.0000000	1.0000000
$\Psi_{1(TTS_0)}$	0.0293356	0.0253935	-0.0128473	-0.0000000	0.0000000	-0.0000000
$\Psi_{1(TS_0T)}$	0.0000229	-0.0000012	0.0000356	-0.0000000	0.0000000	-0.0000000
$\Psi_{1(S_0TT)}$	0.0000144	0.0000295	-0.0000209	0.0000000	-0.0000744	-0.0000042

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AIFDEM EIGEVECTORS IN THE EXCITON-SITE BASIS FOR THE TRIMER IN α WITHIN ENVIRONMENT

Table 5.23 | NOCI coefficients of the MEBFs for each of the states in the DPBF trimer of α within the QM/MM approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Psi_{S[3]}$	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$	$\Phi_{CT[3]}$
$\Psi_{S_0S_0S_0}$	-0.0000000	0.0000000	-0.0000000	0.0000000	-0.0001001	0.0000003
$\Psi_{S_1S_0S_0}$	0.9604347	-0.0000000	-0.0000000	0.0000000	0.0000000	-0.0000000
$\Psi_{S_0S_1S_0}$	-0.0000000	0.9608577	0.0000000	0.0000000	0.0000287	0.0000552
$\Psi_{S_0S_0S_1}$	-0.0000000	0.0000000	0.9608583	-0.0000000	0.0000529	0.0000372
$\Psi_{D_0^+D_0^-S_0}$	0.0000000	0.0000000	-0.0000000	0.0000000	-0.0000458	-0.0000000
$\Psi_{D_0^+S_0D_0^-}$	-0.0000533	0.0000000	0.0000283	-0.0000000	0.0000000	-0.0000000
$\Psi_{D_0^-D_0^+S_0}$	0.0000000	0.0000000	-0.0000000	1.0000000	-0.0000000	-0.0000578
$\Psi_{S_0D_0^+D_0^-}$	-0.0000000	0.0000552	0.0000372	-0.0000578	-0.0000000	1.0000000
$\Psi_{D_0^-S_0D_0^+}$	0.0000373	0.0000000	-0.0000567	-0.0000462	-0.0000000	0.0000000
$\Psi_{S_0D_0^-D_0^+}$	0.0000000	0.0000287	0.0000529	-0.0000000	1.0000000	-0.0000000
$\Psi_{1(TTS_0)}$	0.0000000	-0.0000000	-0.0000000	0.0000000	-0.0000000	-0.0000000
$\Psi_{1(TS_0T)}$	0.0000000	-0.0000000	-0.0000000	0.0000000	-0.0000000	-0.0000000
$\Psi_{1(S_0TT)}$	-0.0000000	0.0000000	0.0000000	-0.0000000	-0.000013	0.0000861

AIFDEM EIGEVECTORS IN THE EXCITON-SITE BASIS FOR THE TRIMER IN β IN GAS PHASE

Table 5.24 | AIFDEM coefficients of the MEBFs for each of the states in the DPBF trimer of β in the gas phase. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Psi_{S[3]}$	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$	$\Phi_{CT[3]}$
$\Psi_{S_0 S_0 S_0}$	0.0143643	-0.0062035	-0.0117932	0.0002852	-0.0000001	0.0000000
$\Psi_{S_1 S_0 S_0}$	-0.6578650	-0.3454719	0.6991897	0.0014282	-0.0000007	-0.0000004
$\Psi_{S_0 S_1 S_0}$	0.4226623	0.6110173	0.6994453	0.0023250	0.0000015	-0.0000009
$\Psi_{S_0 S_0 S_1}$	0.6554500	-0.7406173	0.2510053	-0.0000766	-0.0000007	0.0000021
$\Psi_{D_0^+ D_0^- S_0}$	0.0012150	0.0000714	-0.0027949	0.0002872	-0.0000000	0.0008446
$\Psi_{D_0^+ S_0 D_0^-}$	0.0007670	0.0019238	-0.0021050	-0.0000220	0.0007789	0.0000000
$\Psi_{D_0^- D_0^+ S_0}$	-0.0000011	0.0009655	0.0025569	-0.9999957	0.0009816	-0.0000001
$\Psi_{S_0 D_0^+ D_0^-}$	-0.0000011	-0.0000039	-0.0000012	0.0009320	0.9999993	0.0000000
$\Psi_{D_0^- S_0 D_0^+}$	0.0007699	-0.0022476	0.0014872	0.0000429	-0.0000000	0.0010527
$\Psi_{S_0 D_0^- D_0^+}$	-0.0000029	0.0000040	0.0000011	-0.0000003	-0.0000000	0.9999992
$\Psi_{1(TTS_0)}$	0.0000315	0.0000025	-0.0000566	-0.0003826	0.0000000	0.0000020
$\Psi_{1(TS_0 T)}$	-0.0000194	0.0000496	-0.0000290	0.0000002	0.0000004	-0.0000033
$\Psi_{1(S_0 TT)}$	-0.0011484	-0.0027377	-0.0021242	0.0000023	-0.00000004	0.0000000

AIFDEM EIGEVECTORS IN THE EXCITON-SITE BASIS FOR THE TRIMER IN β WITHIN ENVIRONMENT

Table 5.25 | NOCI coefficients of the MEBFs for each of the states in the DPBF trimer of β within the QM/MM approach. The largest value(s) is(are) indicated in bold.

MEBF	$\Phi_{S[1]}$	$\Phi_{S[2]}$	$\Psi_{S[3]}$	$\Phi_{CT[1]}$	$\Phi_{CT[2]}$	$\Phi_{CT[3]}$
$\Psi_{S_0 S_0 S_0}$	-0.0000105	0.0000015	-0.0000307	-0.0000000	-0.0000000	-0.0000003
$\Psi_{S_1 S_0 S_0}$	0.0000477	0.0000384	1.0204279	-0.0000004	-0.0000000	-0.0000002
$\Psi_{S_0 S_1 S_0}$	1.0206066	-0.0000000	-0.0000477	-0.0000000	0.0000000	-0.0000002
$\Psi_{S_0 S_0 S_1}$	-0.0000000	1.0206080	-0.0000384	0.0000002	0.0000000	-0.0000000
$\Psi_{D_0^+ D_0^- S_0}$	0.0000504	0.0000000	0.0000295	0.0000003	-0.0009080	-0.0000001
$\Psi_{D_0^+ S_0 D_0^-}$	-0.0000000	0.0000252	-0.0000333	-0.0000006	0.0000000	-0.0000003
$\Psi_{D_0^- D_0^+ S_0}$	0.0000345	-0.0000000	0.0000251	-0.0000000	-0.0000000	-0.9999998
$\Psi_{S_0 D_0^+ D_0^-}$	0.0000000	0.0000000	-0.0000000	-0.0000000	0.0000000	0.0004648
$\Psi_{D_0^- S_0 D_0^+}$	-0.0000000	0.0000306	-0.0000507	0.9999982	0.0005785	-0.0000000
$\Psi_{S_0 D_0^- D_0^+}$	-0.0000000	-0.0000000	0.0000000	-0.0006079	0.9999995	-0.0000000
$\Psi_{1(TTS_0)}$	-0.0000000	0.0000000	-0.0000000	-0.0000000	0.0000001	-0.0002604
$\Psi_{1(TS_0 T)}$	-0.0000000	0.0000000	-0.0000000	-0.0020380	-0.0000001	-0.0000000
$\Psi_{1(S_0 TT)}$	-0.0000001	-0.0000000	0.0000000	0.0000000	0.0000000	-0.0000000

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SUMMARY

Conversion of sunlight into electricity prevails, until this day, as a promising source of renewable energy. Nevertheless, enhancement of conversion efficiencies in photovoltaic devices is desired. Different alternatives to boost this efficiency have been explored and applied. Among these alternatives, it has been proposed that the deposition of a layer of a material exhibiting singlet fission (SF) on top of a solar cell could increase its efficiency. This layer has two purposes: to absorb high-energy incident photons that in current solar cells would be lost due to thermalisation, and to potentially generate two pairs of charge carriers per single absorbed photon. Even though experimental attempts to demonstrate the potential of SF materials have been performed in recent years, two main drawbacks still limit their implementation: the small number of molecules known to exhibit SF and limited knowledge on how the process actually occurs.

The aim of this thesis is, aided by computational techniques and theoretical methods, to offer insights in the SF process and attempt to provide answers to the drawbacks mentioned above. We focus on finding novel SF molecules and on providing a deeper understanding on how the process occurs. The basic concepts regarding SF are discussed in **chapter 1**.

In **chapter 2**, we propose 2-methylene-2H-indene as a potential SF chromophore from a set of candidate molecules. Such identification was made based on excitation energies calculated with a variety of electronic structure methods ranging from time-dependent functional theory (employing different functionals) as well as wave function-based methods. Non-orthogonal configuration interaction (NOCI) calculations on selected possible dimer structures of this chromophore suggest that it has the potential to be used in SF applications, and that the process follows a charge transfer(CT)-mediated superexchange mechanism. Additionally, we have compared our NOCI results against two other commonly used methods in the description of SF: the *ab initio* Frenkel-Davydov exciton model and restricted active space method with double spin flip. We conclude that the three methodologies show the same qualitative behaviour and are able to distinguish between dimer conformations with high and low SF probabilities.

Chapter 3 presents a comparison of electronic couplings calculated for 48 pair geometries of cibalackrot, an indigo derivative, with an *ab initio* methodology and a frontier orbital approach. The frontier orbital approach revealed that the SF rates are maximised for these geometric dispositions of the molecules. Our results show a qualitative agreement between the two approaches. Based on the couplings, both approaches agree that one conformation (slip-stacked) is predicted as the most efficient arrangement where SF can occur. The couplings also suggest two additional pair geometries where SF is expected to be efficient. Couplings of the remaining 45 structures are rather similar between each other and no discrimination could be done. The findings of this chapter suggest that the frontier orbital procedure can be used, at first, for the exhaustive screening of pair geometries where the couplings and SF rate are maximised. Then, further investigation

of these pairs can be done by employing a higher level of theory. Based on these studies, structural modifications can be proposed to modify the molecular packing on a crystal and hence, suppress competing processes and enhance the SF process.

In **chapter 4**, we explore the SF process from another point of view. We employ excited-state analysis to characterise and study the singlet excited states of tetracene in monomeric and dimeric forms. We investigated the role of CT states on the SF process. Our study for the monomer reveals that CAM-B3LYP shows the best overall agreement against wave function-based methods in terms of exciton energies and the so-called exciton descriptors. We explore three tetracene dimers, identified within the crystal structure, with different electronic couplings and relative orientations. Our results suggest the presence of resonance states in the dimer with low SF probability whereas local excitons and charge transfer states are observed in those pairs with higher SF probability. Additionally, based on the so-called exciton descriptors, we speculate that the excitons formed in dimers with high SF probability have a weaker Coulombic attraction and hence, can undergo easily the SF process.

Finally, in **chapter 5** we study the effect of the crystal packing in the SF process. Theoretical modelling of SF is often done by employing a gas-phase dimer model, the minimal system where SF can occur. This model has shown its utility to investigate this process, but it does not always cover all the physics and the effect of the environment has to be included in such cases. We study the effect of the crystal packing on (1) the charge transfer-mediated electronic couplings between the S_0S_1 and 1TT states calculated with our NOCI approach, and (2) the excited state character of different arrangements within the crystal structure. Since in reality the process takes place in the crystalline solid phase, knowing how the coupling gets affected by the crystal environment becomes crucial. In this chapter, we study two chromophores known to exhibit SF: tetracene and 1,3-diphenylisobenzofuran (DPBF). The latter is of particular interest since it crystallizes in two different polymorphs with one of them exhibiting a much higher SF efficiency than the other one. Our study reveals that for DPBF the gas phase dimer model is not sufficient and that a trimeric model and inclusion of crystal packing is needed. We also show how the excited state analysis can be used to explain the rather SF yields of the two polymorphs in DPBF.

SAMENVATTING

Het omzetten van zonlicht in elektriciteit wordt tot op vandaag gezien als een veelbelovende bron van hernieuwbare energie. Desondanks is verbetering van of omzettingsefficiëntie efficiëntie in fotonvoltaïsche apparaten gewenst. Verschillende alternatieven om deze efficiëntie te verhogen zijn onderzocht en toegepast. Het is voorgesteld dat het plaatsen van een laagje singlet fission (SF) materiaal op een zonnecel de efficiëntie hiervan zou kunnen verhogen. Deze laag heeft twee doelen: het absorberen van hoog energetische binnenkomende fotonen die in hedendaagse zonnecellen verloren zouden raken door thermalisatie, en het mogelijk genereren van twee paren ladingsdragers voor elk geabsorbeerd foton. Hoewel er in afgelopen jaren experimentele pogingen zijn gedaan om de potentie van SF materialen te demonstreren, zijn er nog steeds twee voornaam nadelen die hun implementatie limiteren: het kleine aantal moleculen waarvan bekend is dat ze SF kunnen laten zien, en beperkte kennis rondom de feitelijke werking van het proces.

Het doel van dit proefschrift is om, met behulp van computationele technieken en theoretische methodes, inzicht te krijgen in het SF proces en om oplossingen te bieden voor de nadelen die hierboven genoemd werden. We focussen op het vinden van nieuwe SF moleculen en op het voorzien van een dieper begrip van de werking van het proces. De basisconcepten rondom SF worden besproken in **hoofdstuk 1**.

In **hoofdstuk 2** stellen we 2-methyleen-2H-indeen voor als mogelijk SF chromofoor uit een set van kandidaat moleculen. Deze identificatie werd gemaakt gebaseerd op excitatie energieën die werden berekend met een aantal elektronische structuur methoden zoals excitatie (waarbij verschillende functionalen zijn gebruikt) en op golf functie gebaseerde methoden. Niet orthogonale configuratie interactie (NOCI) berekeningen op enkele mogelijke dimeer structuren van dit chromofoor suggereren dat het de potentie heeft om gebruikt te worden in SF toepassingen, en dat het proces een door ladingsoverdracht (CT) gefaciliteerd bemiddeld superexchange mechanisme volgt. Daarnaast hebben we onze NOCI resultaten vergeleken met twee andere algemeen gebruikte methoden in het beschrijven van SF: het ab initio Frenkel-Davydov exciton model en de restricted active space methode met dubbele spin flip. We concluderen dat de drie methoden hetzelfde kwalitatieve gedrag vertonen, en zijn in staat om dimeer conformaties met hoge en lage SF waarschijnlijkheid te onderscheiden.

Hoofdstuk 3 presenteert een vergelijking van elektronische koppelingen berekend voor 48 paar geometrieën van cibalackrot, een afgeleide van indigo, met een ab initio methode en een frontier orbitaal benadering. De frontier orbital benadering toonde aan dat de mate van SF gemaximaliseerd is voor deze geometrische disposities van de moleculen. Onze resultaten tonen een kwalitatieve overeenkomst tussen de twee benaderingen. Gebaseerd op de koppelingen tonen beide benaderingen dat één conformatie (slip-stacked) verwacht wordt als de meest efficiënte rangschikking waar SF plaats kan vinden. De koppelingen suggereren ook dat er twee bijkomende paar geometrieën zijn

waar van verwacht wordt dat SF efficiënt is. Koppelingen van de overige 45 structuren zijn tamelijk vergelijkbaar, en er kon verder geen onderscheid gemaakt worden. De bevindingen van dit hoofdstuk suggereren dat de frontier orbital procedure aanvankelijk gebruikt kan worden voor het doorlichten van paar geometrieën waar de koppelingen en SF opbrengst maximaal zijn. Daarna kunnen deze paren verder worden onderzocht door het gebruiken van een hoger niveau van theorie. Gebaseerd op deze studies kunnen structurele modificaties worden voorgesteld om de moleculaire pakking van een kristal te veranderen, om zo de concurrerende processen te onderdrukken en het SF proces te verbeteren.

In **hoofdstuk 4** onderzoeken we het SF proces vanuit een andere hoek. We gebruiken een aangeslagen toestand analyse om de singlet aangeslagen toestanden van tetraceen in monomerische en dimerische vormen te bestuderen en karakteriseren. We onderzochten de rol van CT toestanden in het SF proces. Onze studie voor het monomeer toont aan dat CAM-B3LYP, wat betreft exciton energieën en de zogenoemde exciton beschrijvingen, algeheel de beste overeenkomst vertoont met op golf functie gebaseerde methoden. We onderzoeken drie tetraceen dimeren, geïdentificeerd binnen de kristalstructuur, met verschillende elektronische koppelingen en relatieve oriëntaties. Onze resultaten suggereren de aanwezigheid van resonerende toestanden in het dimeer met lage SF waarschijnlijkheid. Daarnaast, gebaseerd op de zogenoemde exciton beschrijvingen, speculeren we dat de excitonen die gevormd worden in dimeren met hoge SF waarschijnlijkheid, een zwakkere Coulombische aantrekking hebben en zo dus makkelijker het SF proces kunnen ondergaan.

Tot slot bestuderen we in **hoofdstuk 5** het effect van de kristal pakking in het SF proces. Het theoretisch modelleren van SF is vaak gedaan door het gebruiken van een gasfase dimeer model, het minimale systeem waarin SF plaats kan vinden. Dit model heeft zichzelf nuttig bewezen bij het onderzoeken van dit proces, maar het dekt niet altijd alle natuurkunde en het effect van de omgeving moet inbegrepen worden in zulke gevallen. We bestuderen het effect van de kristal pakking op (1) de ladingsoverdracht gefaciliteerde elektronische koppelingen tussen de S_0S_1 en 1TT toestanden berekend met onze NOCI benadering, en (2) de aangeslagen toestandskarakter van verschillende rangschikkingen binnen de kristalstructuur. Omdat in realiteit het proces plaatsvindt in de kristallijne vaste fase, is het cruciaal om te weten hoe de koppeling wordt beïnvloed door de kristallijne omgeving. In dit hoofdstuk onderzoeken we twee chromoforen die SF ondergaan: tetraceen en 1,3-diphenylisobenzofuran (DPBF). De laatste is van bijzonder belang omdat het kristalliseert in twee verschillende polymorfen, waarvan één een veel hogere SF efficiëntie heeft dan de ander. Onze studie toont aan dat voor DPBF het gasfase dimeer model niet voldoende is, en dat een trimeer model en inclusie van kristal pakking nodig zijn. We tonen ook aan hoe de aangeslagen toestand analyse gebruikt kan worden om de uiteenlopende SF opbrengsten van de twee DPBF polymorfen uit te leggen.

LIST OF PUBLICATIONS

8. L. E. Aguilar Suarez, R. Seen, S. Sami, A. Dreuw, S. Faraji. *Solvent models applied to the solvatochromic properties of 2- and 4-pyridiniophenoxides, in preparation.*
7. L. E. Aguilar Suarez, C. de Graaf, S. Faraji. *Influence of the crystal packing in singlet fission: one step beyond the gas phase approximation*, *Phys. Chem. Chem. Phys.* DOI: 10.1039/D1CP00298H.
6. L. E. Aguilar Suarez, M F S. J. Menger, S. Faraji. *Singlet fission in tetracene: an excited state analysis*, *Mol. Phys.* **2020**, 118, e1769870.
5. T. P. Straatsma, R. Broer, S. Faraji, R. W. A. Havenith, L. E. Aguilar Suarez, R. K. Kathir, M. Wibowo, C. de Graaf *GronOR: Massively parallel and GPU-accelerated non-orthogonal configuration interaction for large molecular systems*. *J. Chem. Phys.* **2020**, 152, 064111.
4. L. Luo, T. P. Straatsma, L. E. Aguilar Suarez, R. Broer, D. Bykov, E. F. D'Azevedo, S. S. Faraji, K. C. Gottiparthi, C. de Graaf, J. A. Harris, R. W. A. Havenith, H. J. Aa. Jensen, W. Joubert, R. K. Kathir, J. Larkin, Y. Li, D. I. Lyakh, O. E. B. Messer, M. R. Norman, J. C. Oefelein, R. Sankaran, A. F. Tillack, A. L. Barnes, L. Visscher, J. C. Wells, M. Wibowo, *Pre-exascale accelerated application development: the ORNL Summit experience*, *IBM J. Res. Dev.* **2019** 64,11:1-11:21
3. J. L. Ryerson, A. Zaykov, L. E. Aguilar Suarez, R. W. A. Havenith, B. R. Stepp, P. I. Dron, J. Kaleta, A. Akdag, S. J. Teat, T. F. Magnera, J. R. Miller, Z. Havlas, R. Broer, S. Faraji, J. Michl, J. C. Johnson *Structure and photophysics of indigoids for singlet fission: Cibalackrot*. *J. Chem. Phys.* **2019**, 151, 184903.
2. M. Golkaram, L. Boetje, J. Dong, L. E. Aguilar Suarez, C. Fodor, D. Maniar, E. van Ruymbeke, S. Faraji, G. Portale, K. Loos. *Supramolecular Mimic for Bottlebrush Polymers in Bulk*, *ACS Omega*. **2019**, 4, 16481-16492.
1. L. E. Aguilar Suarez, R. K. Kathir, E. Siagri, R. W. A. Havenith, S. Faraji. *Determination of electronic couplings in the singlet fission process using a nonorthogonal configuration interaction approach*, *Adv. Quantum Chem.* **2019**, 79, 263-287.

CURRICULUM VITÆ

Luis Enrique AGUILAR SUAREZ

04-08-1992 Born in Tenancingo, Mexico.

EDUCATION

- 2017-present **PhD student in Theoretical Chemistry**
Theoretical Chemistry group, Zernike Institute of Advanced Materials
University of Groningen (The Netherlands)
Thesis title: Theoretical Modelling of the singlet fission process: from the gas phase to the inclusion of the environment.
Thesis submitted. Expected graduation date: September 17th, 2021
- 2015-2017 **European Master in Theoretical Chemistry and Computational Modelling**
University of Groningen (The Netherlands), University of Valencia (Spain)
Thesis title: Theoretical study of hole and electron transfer in p-quinquephenyl dimers: a conformational analysis.
Grade: 7.9/10
- 2010-2015 **Bachelor of Science in Chemistry**
Autonomous University of the State of Mexico (Mexico)
Thesis title: In silico study of calix and thia-calix[n]arenes as carriers for Bosutinib and Sorafenib.
Grade: 9.5 /10 (cum laude, Best student fo the 2010-2015 generation)

AWARDS AND RECOGNITIONS

2020	LatinXChem: Honourable mention poster award (online conference, Latin America).
2020	FameLab competition: regional finalist (Groningen, The Netherlands).
2018	FameLab competition: regional finalist (Groningen, The Netherlands).
2017	Roche Continents: Awarded as one of the Top 100 Master science students in Europe. (Salzburg, Austria).
2016	International Genetically Engineered Machine (iGEM) competition (Boston, USA).
Member of the team representing the University of Groningen.
Winners of the Best Information Processing Project track
Nominated for Best Education and Public Engagement
2015	TCCM Master Program: Full Erasmus Mundus scholarship for two years (Tuition and stipend).
2015	Prize "Ignacio Manual Altamirano": Best student of the 2010-2015 generation in the Faculty of Chemistry. (Toluca, Mexico).
2010	CONACyT: Full scholarship to study the Bachelor in Science for five years (Tuition and stipend).
2010	National Mexican Chemistry Olympiad: Second place (silver medal) in B category (Veracruz, Mexico).

ORAL CONTRIBUTIONS IN NATIONAL AND INTERNATIONAL CONFERENCES/ADVANCED SCHOOLS

2021	KNVC-CTC Symposium, Dutch Theoretical Chemistry conference, online, The Netherlands
2020	Invited talk at the Quantum Chemistry group at University of Rovira i Virgili, Spain.
2020	Physics@Veldhoven, Dutch Physics conference. The Netherlands.
2019	International Meeting on Atomic and Molecular Physics and Chemistry. Spain.
2019	Zernike Institute for Advance Materials Meeting. The Netherlands.
- (Not listed here are 12 poster presentations in various national and international conferences/advanced schools)*

ORGANISATIONAL ACTIVITIES OF CONFERENCES AND EVENTS

2021	Local Committee, High Dimensional Quantum Dynamics conference, Groningen, The Netherlands (postponed).
2021	Zernike Day Meeting of the Zernike Institute of Advanced Materials, online, The Netherlands.
2019	Biennial Zernike Institute for Advanced Materials Meeting, Vlieland, The Netherlands.
2017-2021	Group meeting of the Theoretical Chemistry group at University of Groningen, Groningen, The Netherlands.
2013-2015	Co-organiser of the Chemistry Olympiad of the State of Mexico, State of Mexico, Mexico.

PERSONAL SKILLS AND COMPETENCES

Programming languages	Python, Bash, Fortran, C++
Spoken languages	Spanish (native), English (C2), Dutch (B1), Portuguese (B1)
Scientific software	Q-Chem, OpenMolcas, CRYSTAL, DALTON, Gamess-UK, Gaussian, GROMACS.

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