

# Interchromophoric Twist: Gateway to Long-Lived Excitons



*Sohan D. Jadhav*

Sohan D. Jadhav is pursuing an integrated BS-MS degree at the Indian Institute of Science Education and Research Thiruvananthapuram (IISER TVM), where he is conducting research with Prof. Mahesh Hariharan. His research interests lie in understanding various photophysical phenomena and the underlying structure-property relations in organic chromophoric systems. He is a recipient of the Kishore Vaigyanik Protsahan Yojana (KVPY) Fellowship, an undergraduate fellowship awarded to aspiring young, talented researchers in the country.



*Philip Daniel Maret*

Philip Daniel Maret is currently pursuing his integrated PhD course with Prof. Mahesh Hariharan at the Indian Institute of Science Education and Research Thiruvananthapuram, Kerala, India. His research interests focus on to explore the excited state dynamics in chiral organic chromophores using single-molecule spectroscopy.



*Mahesh Hariharan*

Mahesh Hariharan is a Professor in the School of Chemistry, IISER Thiruvananthapuram. After completing his doctoral research (2002–2007) from CSIR-NIIST India with Prof. Danaboyina Ramaiah, Prof. Hariharan carried out his postdoctoral research (2007–2009) with Prof. Frederick D. Lewis at Northwestern University. Prof. Hariharan's research efforts focus on understanding the interaction of light with biomolecules and crystalline and twisted organic materials. Prof. Hariharan is the recipient of the Chemical Research Society of India Bronze Medal (2020), the Japanese Photochemistry Association Lectureship Award for Asian and Oceanian Photochemist Sponsored by Eikohsha (2020), the Distinguished Lectureship Award from the Chemical Society of Japan (2017), and the Asian and Oceanian Photochemistry Association Young Scientist Prize (2014). He was also elected as a Fellow of the Indian Academy of Sciences in 2022.



By Sohan D. Jadhav, Philip Daniel Maret and Mahesh Hariharan\*

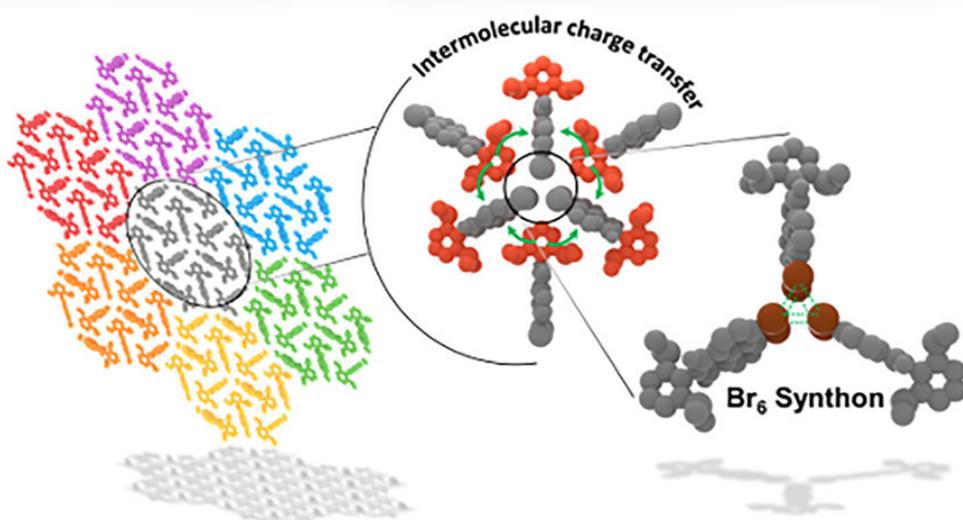
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Structure-property-function relationships play a key role in governing physical properties in molecules and materials in the broader sense. Particularly in organic light-harvesting materials, the sensitivity is magnified as the vibronic and electronic energy landscapes are highly sensitive to the type and extent of quantum chemical communication between molecules. In this article, we select a particular geometric feature- the interchromophoric twist and discuss its implication on several fundamental photophysical properties in connection with our lab's research interests. We highlight two important processes, singlet fission (SF) and symmetry-breaking charge separation (SB-CS). We narrate how the interchromophoric rotation angle can be a crucial tool in achieving an appropriate electronic coupling in each of the cases and help us utilize these processes to achieve long-lived excitons (triplets and unbound electron-hole pairs) for the design and development of efficient artificial solar energy systems.



## Introduction

Energy is crucial for the existence of any living entity. Nature relies heavily on solar rays that are harvested efficiently to fulfil its day-to-day activities, ranging from photosynthesis in plants to Vitamin D production in the human body. Harvesting solar energy is essential as it is renewable and abundant. Moreover, it is necessary to utilise this natural resource to replace fossil fuels with sources of energy free from greenhouse gas emissions. To effectively harness this energy, materials with considerable absorption in the solar spectrum, lower heat dissipation, effective charge separation and large-scale processability are valued. Conventional solar cells are considered quite effective but silicon-based materials suffer from Shockley–Queisser limit and the efficiency of harvesting cannot be pushed beyond this limit.<sup>1</sup> Perovskite-based materials are a new hope with increased efficiency, but most of these suffer from being non-biodegradable.



**Figure 1.** Symmetric radial assembly of chromophores composed of a hexabromine ( $\text{Br}_6$ ) interacting synthon, whose lattice structure resembles the chromophoric arrangement in the light harvesting system 2 of purple bacteria. Reproduced from ref. 10 with permission from American Chemical Society, copyright© 2019.

Organic photovoltaics address the nature friendliness issue and a lot of research is being done to design materials to make efficient solar energy harvesters. Nature is an excellent reference to learn how this can be achieved artificially<sup>2,3</sup> and the chromophoric arrangements in nature are quite crucial let it be at the macroscale or nanoscale.

The rational design of chromophores and precise control of intermolecular interactions is crucial for achieving materials that exhibit excellent, desired photophysical properties in a laboratory setting (sometimes a serendipitous discovery). The likelihood of achieving this goal is higher when we have a clear picture of the necessary, favourable molecular packing that can aid a particular process. However, provided this guideline, can we predict the molecular structure and the necessary chemical modifications that will lead to a particular crystal packing? To a certain extent, maybe, through intuition and rigorous synthetic attempts. This question remains a pressing challenge being pursued by the crystal engineering and molecular modelling communities.

In our lab, we use a wide range of techniques from organic synthesis, crystal engineering, spectroscopy and computational chemistry to identify distinct chromophoric systems and architectures exhibiting exciting and emergent photophysical properties.<sup>4-10</sup> In this article, we will focus on a particular intermolecular packing feature- the interchromophoric twist, whose photophysical relevance and importance we are still exploring, and in course, will also touch upon the recent experimental and theoretical reports we have communicated along this line. We first elaborate on the importance of the rotation angle as a tool to fine-tune the interchromophoric interactions and serve as a potentially new design guideline for efficient singlet fission (SF), a current, hot topic of research to better harness solar energy through photon energy conversion. We also include brief discussions on the processes of charge-filtering and symmetry-breaking charge separation (SB-CS) observed in rotated offsets, that can be advantageous for design of optoelectronic and photovoltaic devices.

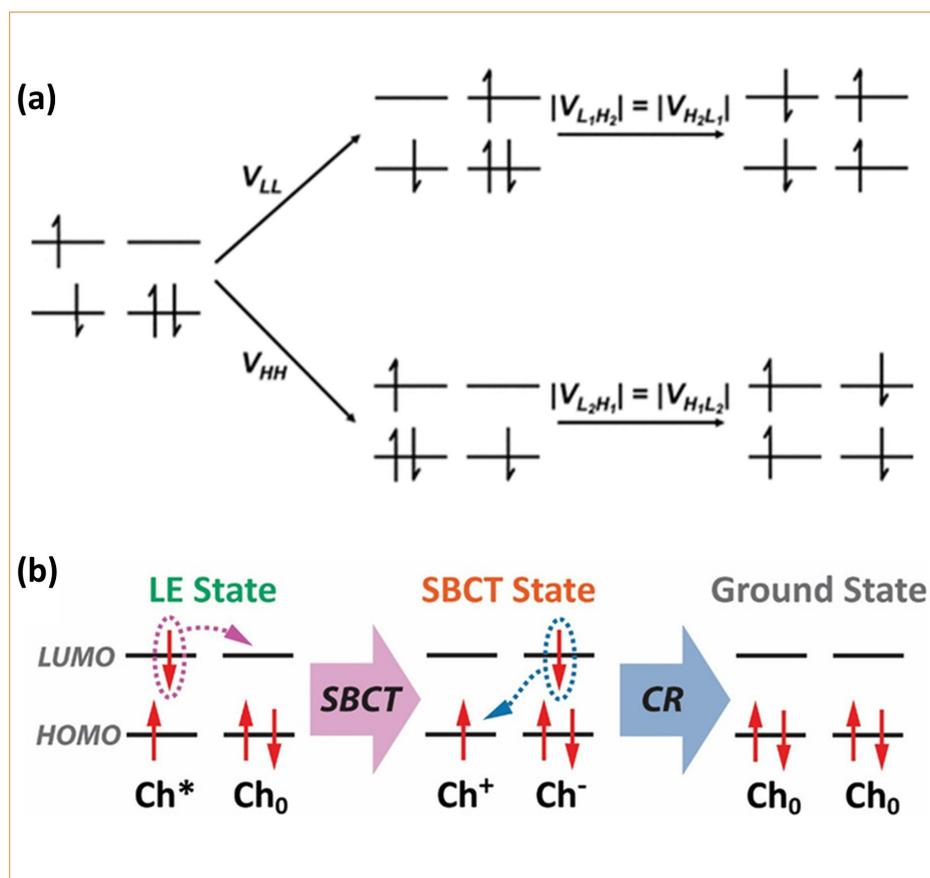
SF is a photophysical, multi-exciton generation (MEG) process in which a singlet exciton is converted into two triplet excitons.<sup>11,12</sup> First observed in tetracene crystals back in 1969,<sup>13</sup> the ability of the process to improve solar cell efficiency has resulted in a growing interest and resurgence in SF. The process has evolved as a strategy to overcome the Shockley-Queisser limit<sup>14-16</sup>, which states that the maximum photoconversion efficiency that can be realized practically

is 33%.<sup>1</sup> This technique of photon energy downconversion can be used to circumvent the issue of mismatching with the broad solar energy spectrum by essentially converting incoming photons of high energy to that which matches the absorption of the photovoltaic device.<sup>17</sup>

Photo-functional materials from various polyaromatic hydrocarbons and their derivatives are engineered using molecular synthesis to harness properties like energy transfer and prolonged charge separation.<sup>2,18-20</sup> Excited state SB-CS in chromophoric pairs with the hole and electron localized on different chromophores can be achieved provided an optimum electronic coupling and potentiometric bandgap.<sup>20</sup> Since the exciton binding energy in the organic systems (> 100 meV) is about 10 times greater than in silicon-based semiconductors (10-20 meV), attaining a prolonged charge-separated state in organic semiconductors is challenging.<sup>20</sup> To this aim, molecular architectures that can attain a prolonged charge separated state and reduce the rate of charge

recombination are crucial for the effective functioning of organic photovoltaics.

In 1965, Kasha and co-workers developed a theoretical relation between photophysical properties and underlying molecular assemblies.<sup>21</sup> Long-range Coulombic coupling was the basis to explain the exciton splitting for various geometrical dimer arrangements. Later on, extensive theoretical efforts by Spano and co-workers revealed the importance of short-range charge-transfer (CT) couplings in addition to the long-range interactions discussed in the Kasha model.<sup>22</sup> The total excitonic coupling ( $J_{eff}$ ) is rather a sum of the Coulombic ( $J_{coul}$ ) and CT-mediated ( $J_{CT}$ ) couplings.<sup>22</sup> The CT-interactions originate from the overlap of highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) of monomers.<sup>22,23</sup> In simpler terms, molecules communicate to one another when in proximity through quantum chemical means, in technical terms, called electronic coupling. The one-electron coupling matrix elements provide significant insights into charge transport



**Figure 2.** (a) Schematic of SF pathway. Horizontal coupling matrix elements connect the initial FE to CT state and the non-horizontal coupling elements connect the CT to TT state. Reproduced from ref. 26 with permission from American Chemical Society, copyright© 2017. (b) Symmetry-breaking charge transfer (SB-CT) in a chromophore (Ch) dimer is dependent on HOMO-HOMO/LUMO-LUMO spatial overlap (horizontal couplings) while charge recombination (CR) is dependent on the HOMO-LUMO spatial overlap (non-horizontal couplings). Reproduced from ref. 27 with permission from American Chemical Society, copyright© 2022.

and electron transfer processes.<sup>24</sup> Assuming the frontier molecular orbitals, HOMO and LUMO are the key participants in the photochemical/physical process, one-electron coupling matrix elements can be classified into two categories. Firstly, the horizontal coupling matrix elements HOMO-HOMO and LUMO-LUMO that correspond to the hole and electron transfer couplings ( $t_h$  and  $t_e$ ) respectively. Next, the non-horizontal coupling matrix elements HOMO-LUMO and LUMO-HOMO, that play a vital role in SF.<sup>25</sup> These one-electron matrix elements  $\langle \phi_1^A | F | \phi_2^B \rangle$  are represented as  $F_{AB}/V_{AB}$  where A and B correspond to the HOMO(H)/LUMO(L) of each individual monomer. The electronic couplings that stem from the interorbital overlap are highly sensitive to relative orientations of chromophores in closely packed systems.<sup>5,22</sup> Figure 2 presents schematics of the role of the charge transfer couplings from the aspect of SF and SB-CS.<sup>26,27</sup>

In a recent study, we theoretically investigated the dependence of the charge transfer coupling on the rotation angle between co-facially-stacked dimeric systems in a series of  $\pi$ -conjugated molecules.<sup>5</sup> We unveiled an interesting optoelectronic property correlation that acene systems exhibit mutually exclusive hole and electron transfer couplings in the Greek cross (+) architecture, whose selectivity is dictated by the symmetry of the frontier molecular orbitals. For  $(4n + 2)$   $\pi$ -electronic acene systems, those with odd (even) number of benzenoids exhibit

exclusive electron (hole) transfer coupling. Fascinatingly, the trend is reversed for the selected  $4n \pi$ -electronic acene systems.<sup>5</sup>

### Singlet Fission

Intermolecular rotation indeed affects the coupling matrix elements, but can this variation be detrimental or conducive for SF? In a recent study, we investigated this question by selecting a terrylene dimer model and evaluating the singlet fission rate as a function of interplanar rotation and long-axis displacement (Figure 4a).<sup>8</sup> We adopted the frontier orbital model theory popularized by Michl et al. to evaluate the SF coupling<sup>11,12</sup> and subsequently applied the effective Hamiltonian SF theory developed by Nakano et al. to account for the effect of CT mixing on the Frenkel exciton (FE) and triplet pair (TT) energy levels.<sup>25,28</sup> The efficiency of singlet fission is dependent on all the coupling matrix elements.<sup>25</sup> It is popularly known that singlet fission is unfavourable in a sandwich stack of  $\pi$ -conjugated chromophores due to null values of the non-horizontal coupling matrix elements, despite the horizontal coupling matrix elements being maximum.<sup>24</sup> Slip-stacking circumvents this hurdle by favouring the HOMO-LUMO interaction between chromophores.<sup>11,24</sup> At the unrotated geometry, the effective SF coupling  $V_{SF}$  is maximised at displacements of 0.6 Å, 2.6 Å and 3.6 Å. In the rotated geometries, maxima are centered at roughly 50° and 65° upon systematically increasing the long-axis displacement (Figure 4b).<sup>8</sup>

Along with potentially making SF faster, competing pathways such as excimer formation are activated at merely slip-stacked configurations.<sup>26,28</sup> Figure 4c represents a map of  $(E'_{FE} - E'_{TT})$ . SF is predicted to be favoured over excimer formation when effective energy of the TT state  $E'_{TT}$  lies below that of the FE state  $E'_{FE}$ .<sup>25</sup> The green regions on the map represent such configurations at which  $E'_{FE} - E'_{TT} \geq 0$ , where exothermal SF is expected to be favourable.<sup>8</sup> In contrary, the presence of multiple non-green regions in the untwisted orientations supports the reported experimental observation of prevalent excimer formation in slip-stacked geometries<sup>26</sup> and the beneficial role of the interchromophoric rotation is evident in overcoming this energetic limitation. To convey a holistic picture of the importance of the rotation angle, we selected two model displacements and looked into the variation of all parameters  $V_{SF}$  and  $E'_{FE/TT}$  in a single plot. We also included the effect of the effective excitonic coupling ( $J_{eff}$ ), that comprises of both the short-range and long-range components that further stabilize  $E'_{FE}$ .<sup>25</sup> A quantitative description of the results along with the equations used to evaluate the rate and energetics are given in ref. 8.

At a displacement of  $x=0.6$  Å, we observe that SF is energetically disfavoured at the unrotated geometry ( $\theta=0^\circ$ ) despite the possibility of fast SF (red region). Large values of horizontal coupling matrix elements combined with maximum electrostatic interactions between the monomers contribute to

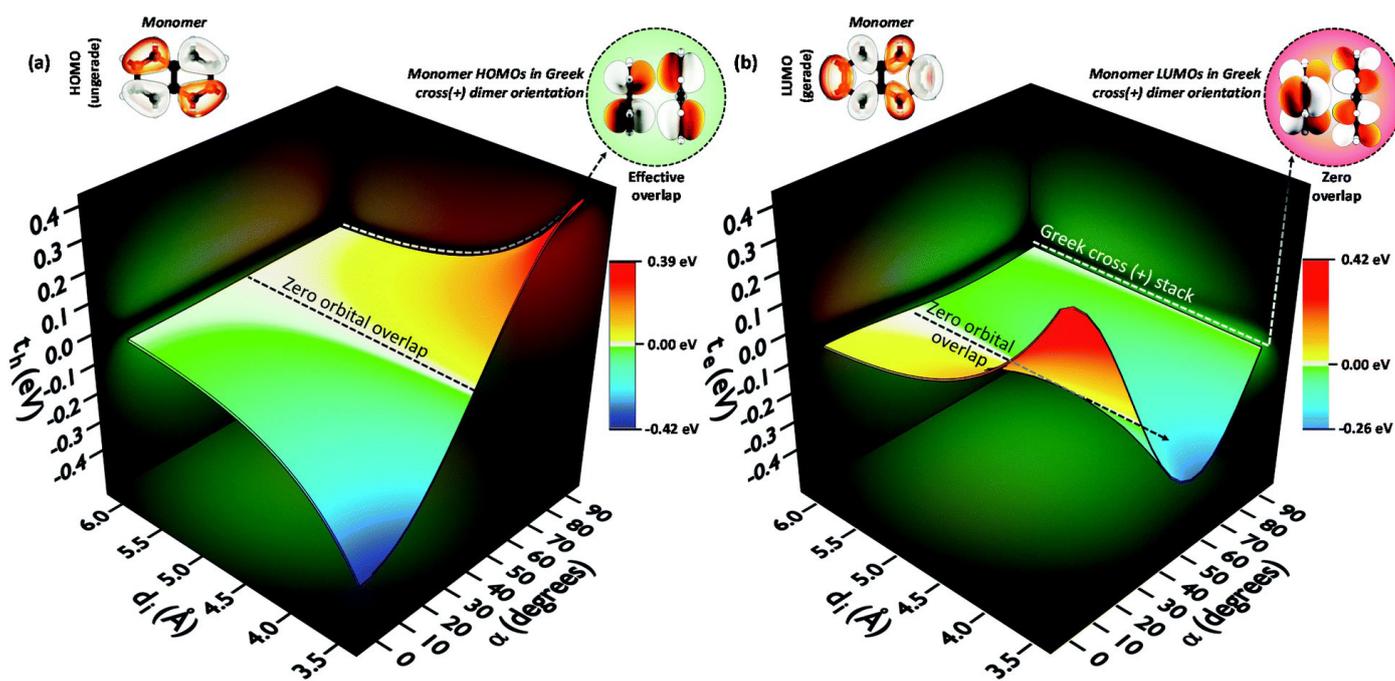


Figure 3. 3D surface plot to understand the correlation of the rotational angle, intermolecular distance and charge transfer integral.<sup>5</sup>

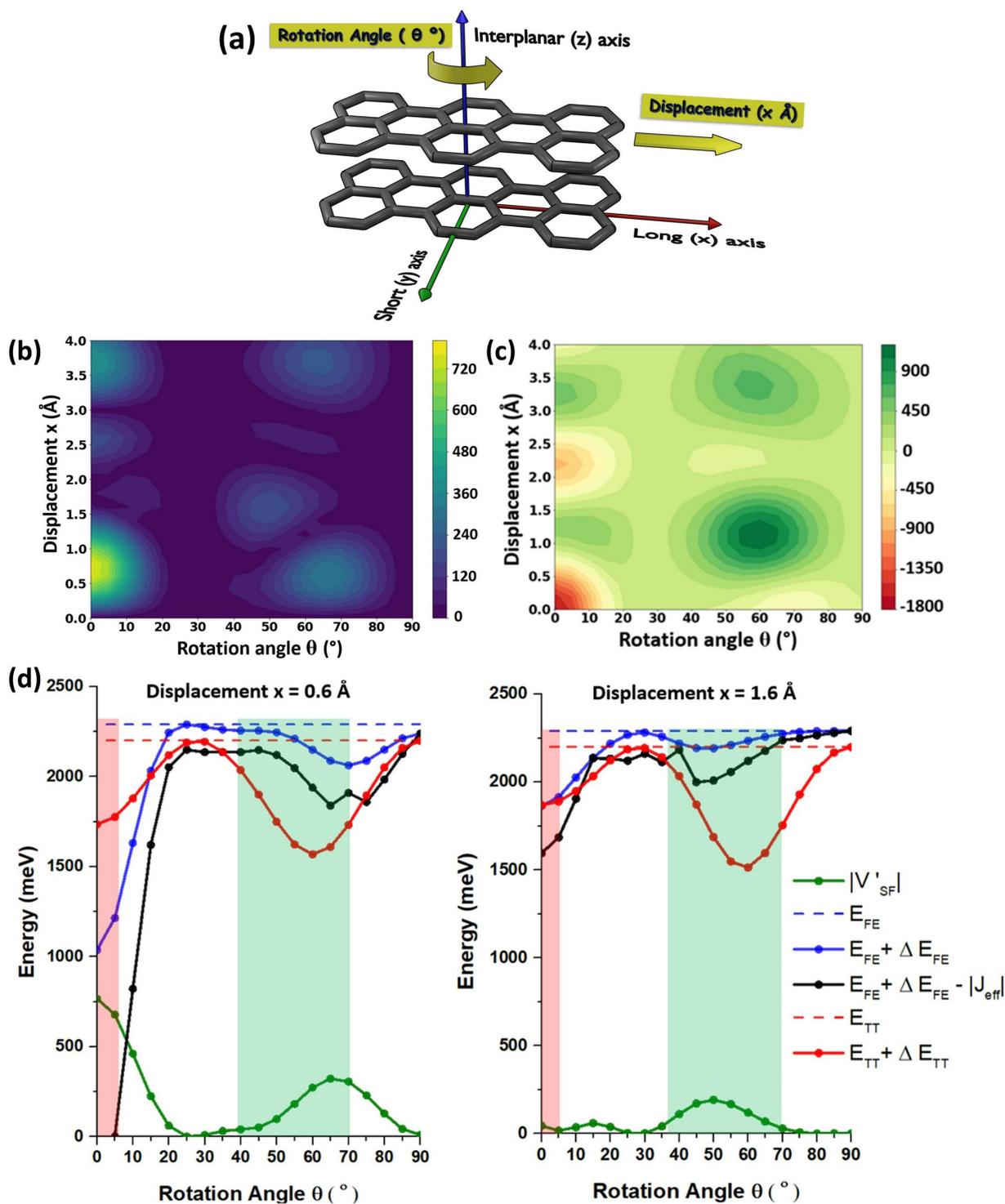


Figure 4. (a) Terrylene dimer model (hydrogens are omitted for ease of representation) (b) Effective SF coupling  $V'_{SF}$  (in meV) as a function of rotation angle and long-axis displacement (c) Difference between effective energies of the FE and TT states following CT-mixing ( $E'_{FE} - E'_{TT}$ ) (in meV) as a function of rotation angle and long-axis displacement (d) Trends of effective SF coupling and effective energetics as a function of rotation angle at displacement of 0.6 Å and 1.6 Å.<sup>8</sup>

the overstabilization of the FE state.<sup>8</sup> Upon inducing rotation, we notice that the energetic stabilization of the FE state decreases with a twist greater than 15°. Furthermore, that TT state is stabilized to a global minimum at  $\theta=60^\circ$  (green region).<sup>8</sup> At another displacement of  $x = 1.6 \text{ \AA}$ , poor  $V'_{SF}$  accompanied with unfavourable energetics indicate that SF is less favourable when  $\theta=0^\circ$  (red

region). Introducing an interplanar twist not only stabilizes the TT state more than the FE state, but also enhances SF coupling nearly 5 times (at  $\theta=50^\circ$ ) compared to the untwisted packing (green region).<sup>8</sup> The two representative examples shed light on how rotation can control the intermolecular packing sensitive parameters that together effect the overall efficiency of SF. This is achieved

through tuning the energetics while maintaining a satisfactory SF rate at optimal twist angles, that ultimately enhances the triplet yield by preventing deactivation pathways through alternate channels such as excimer formation.

Interestingly, our theoretical calculations qualitatively explain the experimentally

observed enhanced triplet yields in slip-stacked, twisted morphologies of various other chromophoric moieties. Wasielewski et al. synthesized two TDI derivatives that packed in distinct crystal morphologies. A triplet yield of 190% was observed in the slip-stacked, twisted arrangement in

contrast to a mere 50% triplet yield in the slip-stacked counterpart due to observed excimer formation.<sup>26</sup> In a different report by Gurzadyan et al. on perylene and its *tert*-butyl substituted derivative (TBP<sub>e</sub>), the former arranged in a face-to-face, twisted assembly and had a triplet quantum yield of 108%,

the triplet quantum yield was improved to 185% in TBP<sub>e</sub> that formed a slip-stacked, twisted assembly due to hindered excimer formation.<sup>29</sup> Furthermore, the significance of the rotation angle was also highlighted by Ananth, Sfeir, Campos and co-workers in the pentacenes that were covalently linked

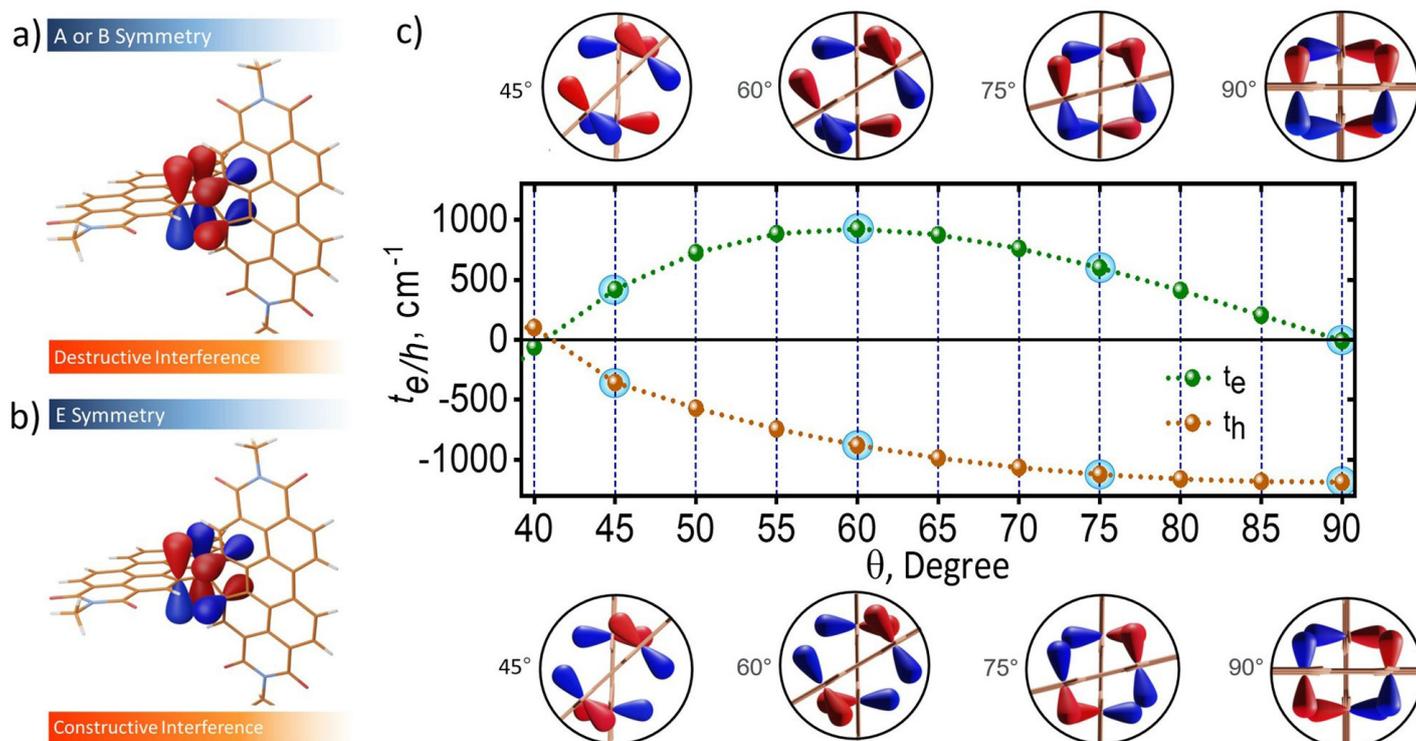
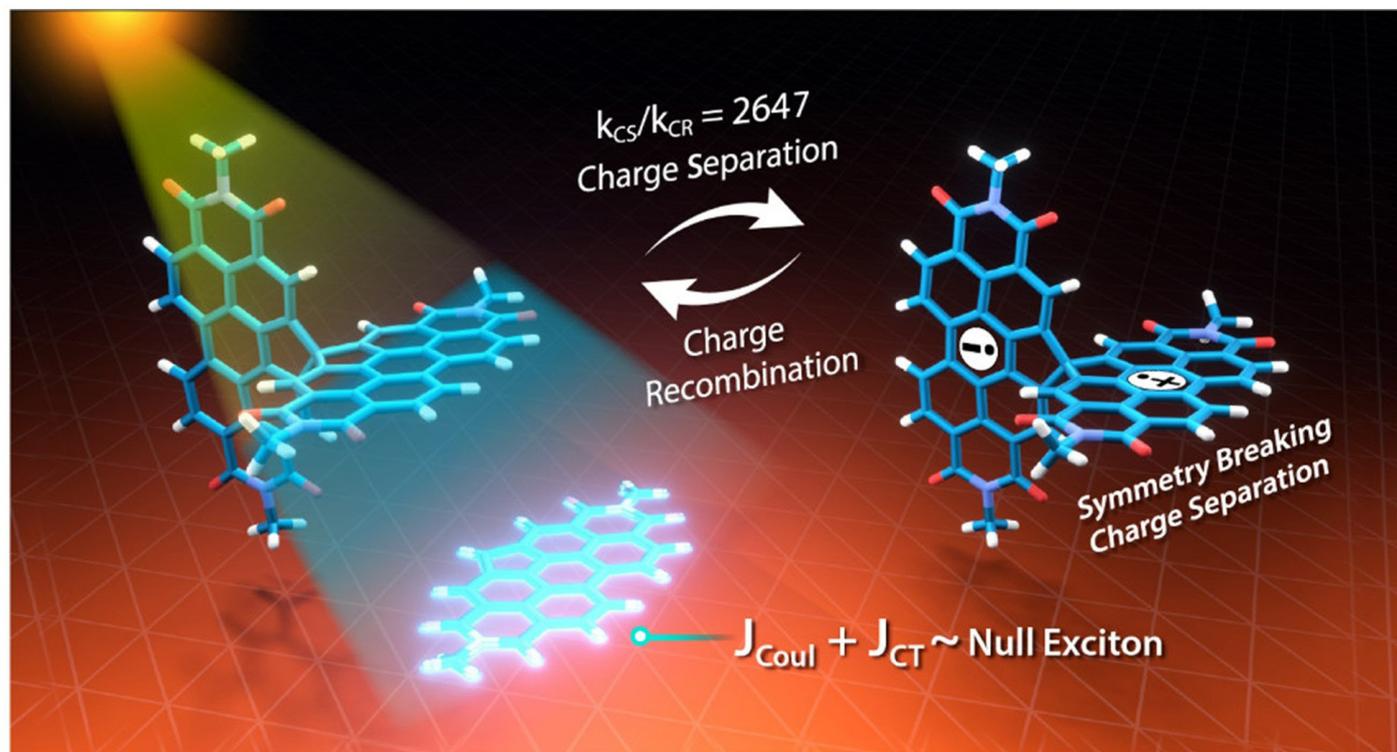


Figure 5. Top: Spiro-bridged perylene diimide dimer having a Greek cross (+) arrangement. Bottom: Constructive and destructive interference of LUMOs and HOMOs (a-b). The dihedral angle dependence on the electron and hole transfer integrals (c). Reproduced from ref. 7 with permission from American Chemical Society, copyright© 2021.

at different positions relative to one another, to achieve dimers with tunable twist angles.<sup>30</sup> These experimental results further corroborate the role of combined twisted and slip-stacked molecular packing arrangements for promoting efficient SF. Moreover, they depict how intermolecular packing can be optimized using interplanar rotation as a beneficial strategy to make the energetics conducive for exothermal SF and improve the rate for practical solar cell applications.

### Symmetry-Breaking Charge Separation

The features that determine whether a particular system will show SB-CS or SF depend on the orientation of the chromophores and interactions between them. SB-CS is yet another process of great interest observed in various dimeric systems.<sup>18,20,27</sup> But how can we achieve an efficient SB-CS in a dimeric system? Here comes the twist! Twisted interchromophoric orientations aren't advantageous for singlet fission alone. From our lab, we recently reported a null exciton-coupled spiro-conjugated perylene diimide dimer (Sp-PDI<sub>2</sub>) exhibiting highly efficient symmetry-breaking charge separation.<sup>7</sup>

Quantum chemical calculations of the charges transfer integrals revealed a high hole-transfer integral ( $t_h$ ) and low electron transfer integral ( $t_e$ ). This implies a constructive interference of HOMOs and destructive interference of LUMOs in the optimised geometry of Sp-PDI<sub>2</sub> as illustrated in Figure 5. The interference between the theoretically calculated Coulombic  $J_{Coul}$  and CT-mediated  $J_{CT}$  couplings resulted in null exciton coupling of the edge-to-edge arranged perylene diimide dimer possessing orthogonal orientation of transition dipoles.<sup>7</sup> Through further experimental studies, we reported the unequivocal evidence for the prolonged SB-CS state (a striking  $k_{CS}/k_{CR} = 2647$  in acetonitrile solvent!) in this PDI-based dimeric system, Sp-PDI<sub>2</sub>.<sup>7</sup>

This work combines two fundamental concepts of photophysics, null exciton splitting and symmetry-breaking charge separation, as a novel strategy to generate long-lived charge-separated states.<sup>7</sup> The Greek cross (+)-arrangement can be considered as an ideal system that highlights the correlation between the relative orientation of the chromophoric system and its orbital interaction in dictating complex excited-state dynamics.<sup>4-7</sup>

The role of spatial separation and mutual orientation of a series of linked dipyrroin chromophores on symmetry-breaking-charge transfer (SB-CT) were investigated by Thompson, Bradforth and coworkers.<sup>27</sup> The role of the horizontal and non-horizontal

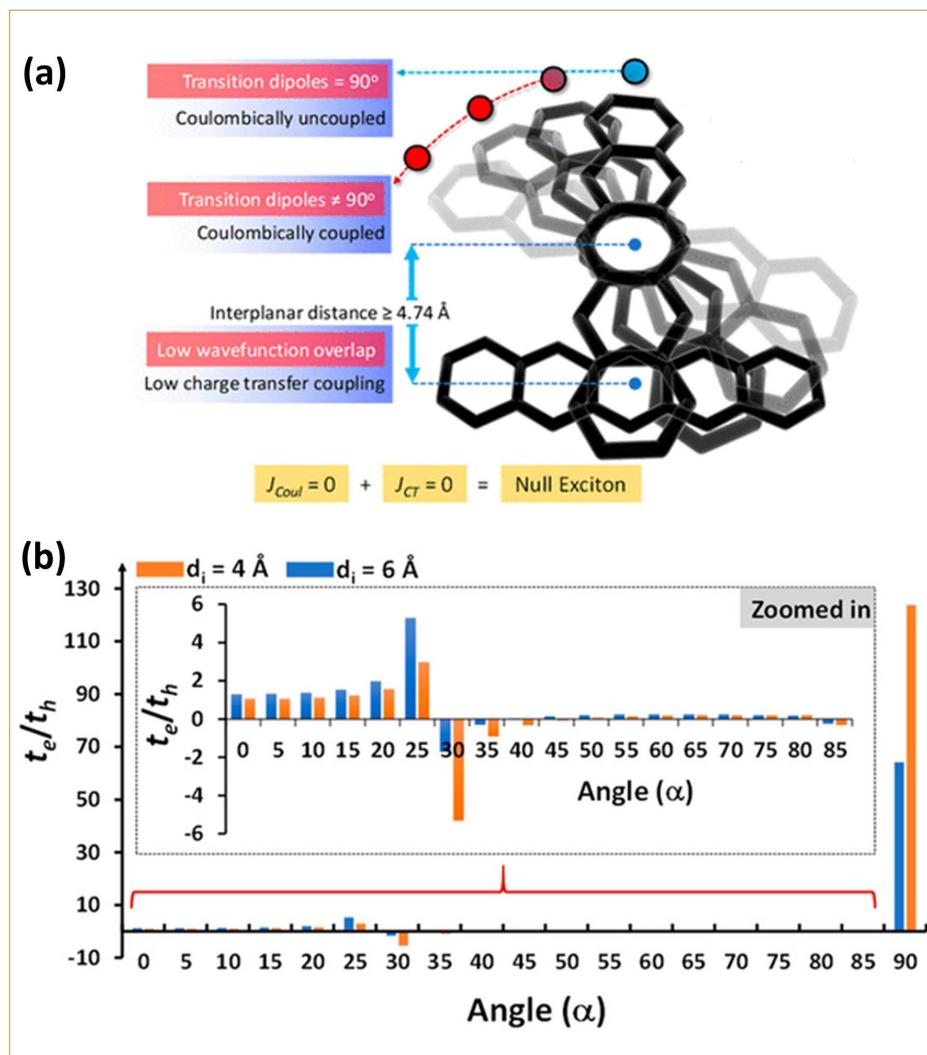
coupling matrix elements were also emphasized on in the article. SB-CS is only a special case of SB-CT in which the electrons and holes are fully decoupled.<sup>27</sup> The rate and longevity of charge separation are strongly governed by the charge transfer integrals that are sensitive to the spatial overlap and symmetry of the HOMO and LUMO of the coupled chromophores. The first step, charge transfer requires adequate overlap between the identical (or horizontal) molecular orbitals i.e., decent HOMO-HOMO or LUMO-LUMO overlap. On the other hand, charge recombination is favoured by the HOMO-LUMO (non-horizontal) coupling matrix elements, intuitively, the orbital overlap between the resultant anion and cation pair.<sup>27</sup>

In the case of boron dipyrromethene (BODIPY) dimers, it was observed that HOMO-HOMO coupling was maximum and

the LUMO-LUMO coupling was minimum at a dihedral angle of 90°, in resemblance with our Sp-PDI<sub>2</sub> system.<sup>27</sup> The authors inferred that SB-CT hole transfer might be taking place in their system but electron transfer is hindered. They further found that the magnitude of LUMO-LUMO coupling increases steeply compared to the decrease in HOMO-HOMO coupling, suggesting that the rate of SB-CT can be improved upon reducing the torsional rigidity in the dimers.<sup>27</sup>

### Charge-filtering

The glory of Greek cross (+)-arrangement doesn't stop at achieving a long-lived charge-separated state. Rotated offsets can also exhibit interesting properties for optoelectronic applications. Not too long ago, to the best of our knowledge, we were the first to report the crystal evidence for null-exciton interaction in the Greek cross (+)-arrangement between substituted



**Figure 6.** (a) The coupling shown in pentacene dimers with rotational offset. (b) The charge filtering feature in the pentacene cross stack with change in rotational angle. Reproduced from ref. 4 with permission from American Chemical Society, copyright© 2020.

perylene that arranged in an orthogonal geometry.<sup>6</sup> In 2020, we also reported a series of substituted pentacenes that crystallized in a distinct Greek cross (+)-architecture and exhibited null exciton interactions.<sup>4</sup> Advanced computational methods were used to examine the crystal structure and excitonic interactions between the chromophores. Interestingly, evaluation of the electronic couplings revealed that these orthogonally-stacked chromophore assemblies exhibited Kasha's ideal null-exciton splitting i.e., negligible contributions from the short-range charge-transfer coupling and long-range Coulombic coupling (Figure 6). Due to suppressed HOMO-HOMO interactions and minimum hole-transfer ( $t_h$ ) coupling in pentacene cross-stack, the system facilitates filtering of the charge-transfer coupling (Figure 6).<sup>4</sup>

## Conclusion

In summary, this article discusses the importance of controlling interchromophoric coupling and in particular, the dependence of the charge-transfer integrals on the rotation angle between chromophores and its implications. In line with the recent developments from our group, we take SF and SB-CS as two examples and demonstrate the importance of inducing the appropriate type and strength of coupling to achieve a satisfactory

efficiency. Moderate, non-zero values of all the four coupling matrix elements favour fast and exothermal SF. However, SB-CS is favoured when the horizontal coupling matrix i.e., either  $t_o$  and  $t_h$  are large enough and the non-horizontal coupling matrix elements are minimum to prevent charge recombination. The relevance of the rotational angle with respect to several fundamental concepts in photophysics, such as null exciton splitting, charge-filtering, singlet fission and symmetry-breaking charge separation are discussed as innovative strategies to generate efficient, long-lived excitons. Further efforts are underway in our laboratory to achieve these properties in twisted and near-orthogonal arranged dimers. All in all, science is all about twists and through this article, we shed light on how the interchromophoric twist can contribute to make better materials for a greener world.



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