Electronic structure of substituted BODIPY dyes : Application to singlet fission

Sophiya Goyal, S. Rajagopala Reddy

Department of Chemistry, Central University of Rajasthan, Ajmer, India

Email: 2020phdch005@curaj.ac.in

Motivation

- Solar energy is a promising way to meet global energy needs.
- The theoretical efficiency limit or Shockley-Queisser limit for Single-junction solar cells is ~33% [1].
- Organic devices made from singlet fission (SF) enabled materials, doubles the efficiency by generating two or more electron-hole pairs by absorption of one photon [2].
- Understanding SF may lead to a knowledge-based design of highly efficient next generation solar cells using environmental friendly and inexpensive SF enabled materials.

Introduction to SF

- Singlet fission (SF) is a spin allowed process that a singlet exciton fission to two triplet excitons [3].
- Its mechanism (direct, mediated or super -exchange) is highly debated.

$$S_0 + S_1 \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} {}^1(TT) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} T_1 + T_1$$

where $^1(T_1T_1)$ is a correlated triplet pair whose wavefunction is a combination of two triplet states coupled to a singlet.

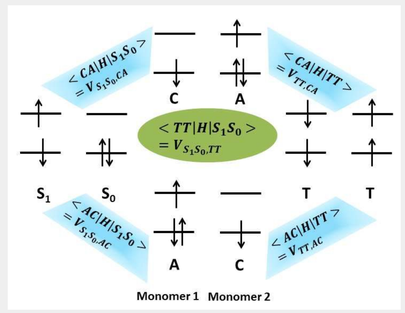
- Energetics of the excited electronic states for SF

$$2E(T_1) - E(S_1) \leq 0$$

$$2E(T_1) - E(T_2) \leq 0$$

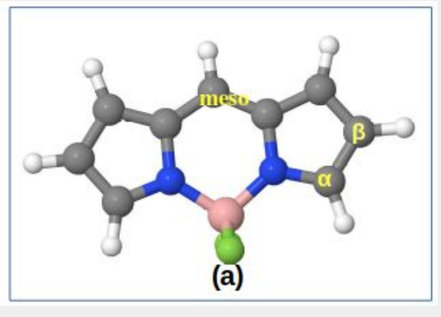
that have to be fulfilled in order to

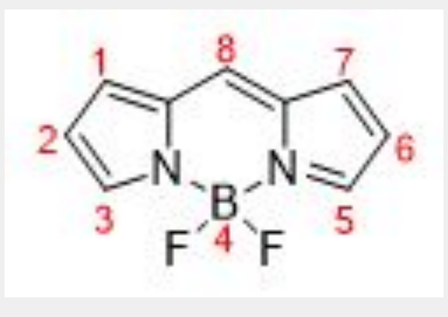
- be able to split a singlet exciton (S_1) into two triplet excitons (T_1)
- suppress triplet-triplet annihilation



Search for a chromophore

- An SF sensitizer must satisfy the above conditions which creates difficulty to perform efficient SF [4] .
- Only a few chromophores can currently undergo SF efficiently [5].
- However, the majority of research has focused on large alternant hydrocarbons.
- Later, interest has been shifted to diradicaloids due to their open shell character, small size and less computation time.
- The term “diradicaloids” refers to species with partial radical character (weak interaction of two separate radicals) [6].
- Diradicals favour the SF as they are inherently unstable and have an open shell character.
- In this contribution, we have chosen BODIPY (4,4-Difluoro-4-bora-3a-4a-diaza-s-indacene) as the chromophore of choice on the design front, to realize the SF enable system due to their various applications [7].





- To study the effect of the substitution on the singlet and triplet energies and hence, we have varied the groups in terms of their π-accepting and π-donating nature and the substitution position (alpha, beta and meso) and calculated the excitation energies [8].

Diradical Character in BODIPY

$$y_i = 1 - \frac{2T_i}{1+T_i^2} \qquad T_i = \frac{n_{HOMO-i} - n_{LUMO-i}}{2}$$

Where i = degree of diradical character

T_i = function of the occupation number of natural orbitals

- y_0 value must be lie between 0.2 and 0.5 for efficient SF [9].

Electronic structure of BODIPY

Optimization: DFT/B3LYP/Def2-TZVP/TURBOMOLE

Excited states and potential energy surfaces (PESs):

SA-CASSCF(л, л*)//XMCQDPT/DZV/GAMESS

RICC2/TURBOMOLE

ORMAS for n-л* transitions

Results and Discussion

- The substitution affects the electron distribution in the molecule in terms of π-accepting and π-donating nature of the groups. Some important groups are BH_2, CF_3, OH, NH_2.
- The best set of substitutions are shown below in the table

	α	β	meso	ΔSF (RICC2)	ΔSF (XMCQDPT)	Y_0 (x100)
1	BH_2	H	H	0.96	1.00	1.67
2	H	NH_2	H	0.79	0.59	4.86
3	BH_2	NH_2	H	0.53	0.57	2.71
4	H	H	CN	0.97	0.68	0.96
5	BH_2	NH_2	CN	0.19	0.30	7.37
5-dimer	BH_2	NH_2	CN	0.35	0.25	16.70

- Dimer constituting monomer 5 show strong diradical character and favorable SF energetics.
- Quantum nuclear dynamics study is underway to understand the SF mechanism in the dimer.

References

1. Shockley, W.; Queisser, H. J. *J. Appl. Phys.* **1961**, *32*, 510.
2. Hanna, M.; Nozik, A. *J. Appl. Phys.* **2006**, *100*, 074510.
3. Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891.
4. Margulies, E. A.; Miller, C. E.; Wu, Y.; Ma, L.; Schatz, G. C.; Young, R. M.; Wasielewski, M. R. *Nat. Chem.* **2016**, *8*, 1120.
5. Burdett, J. J.; Müller, A. M.; Gosztola, D.; Bardeen, C. J. *J. Chem. Phys.* **2010**, *133*, 144506.; Burdett, J. J.; Müller, A. M.; Gosztola, D.; Bardeen, C. J. *J. Chem. Phys.* **2010**, *133*, 144506.
6. Casanova, D. *Chem. Rev.* **2018**, *118*, 7164.
7. Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891.; Barbon, S.; Price, J.; Yogarajah, U.; Gilroy, *J. RSC Adv.*, **2015**, *5*, 56316.
8. Pradhan, E.; Bentley, J. N.; Caputo, C. B. Zeng, T. *ChemPhotoChem* **2020**, *4*, 5279.
9. Yamaguchi, K.; Carbo, R.; Klobukowski, M. Self-consistent field: theory and applications. by R. Carbo and M. Klobukowski, Elsevier, Amsterdam **1990**, 727.

Acknowledgement

DST-SERB/2021/001684 for computational facility.
UGC for Junior Research Fellowship.
Pedro B. Coto for helpful suggestions.