Intersystem Crossing in Boron-Based Donor–Spiro–Acceptor Organic Chromophore: A Detailed Theoretical Study

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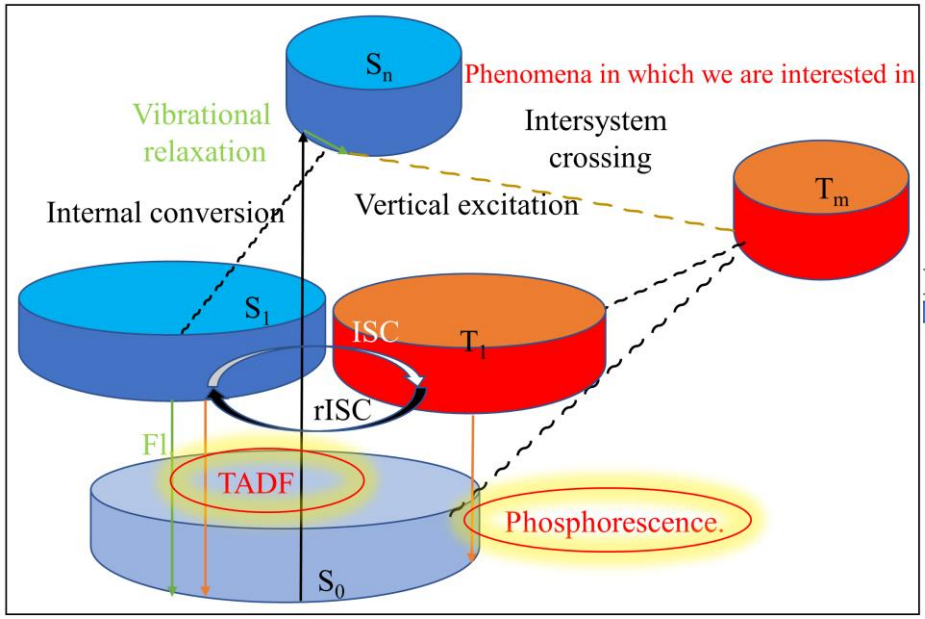
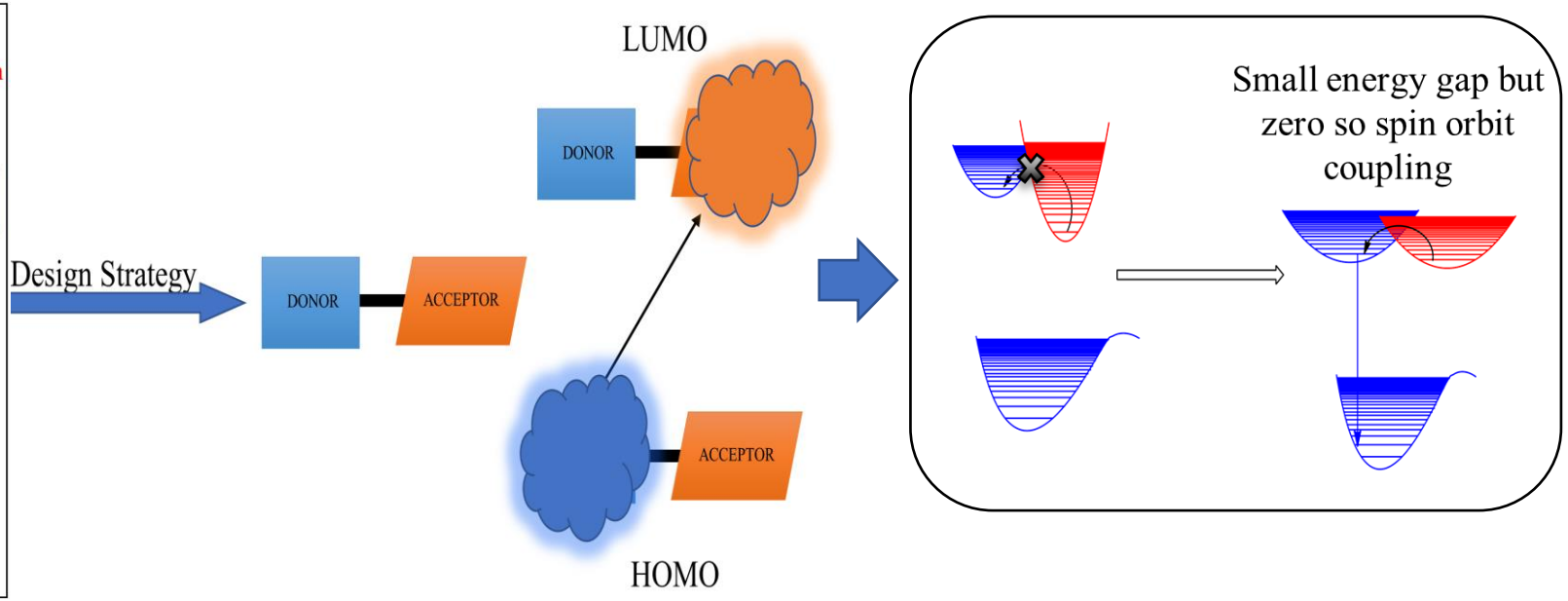
INTRODUCTION:





- Stanoppi, M.; Lorbach, A. Boron-based donor-spiro-acceptor compounds exhibiting thermally activated delayed fluorescence (TADF).Dalton Transactions2018,47, 10394–10398.
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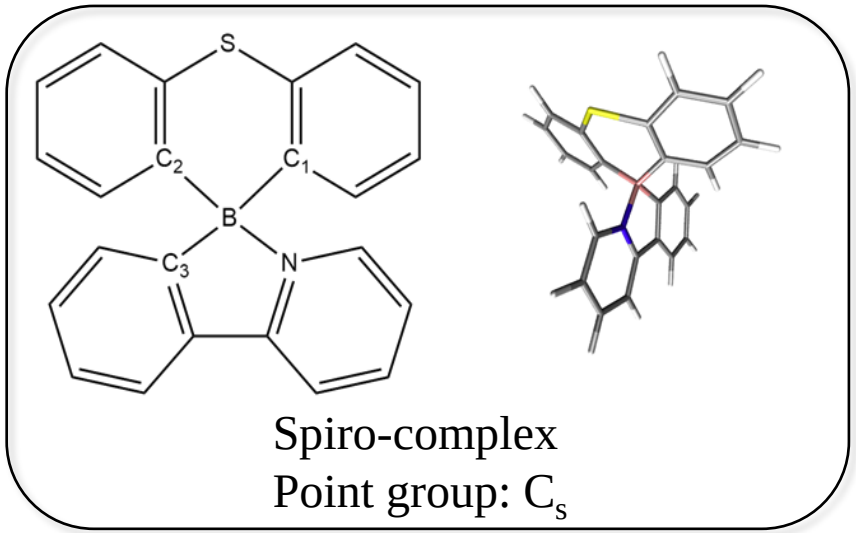
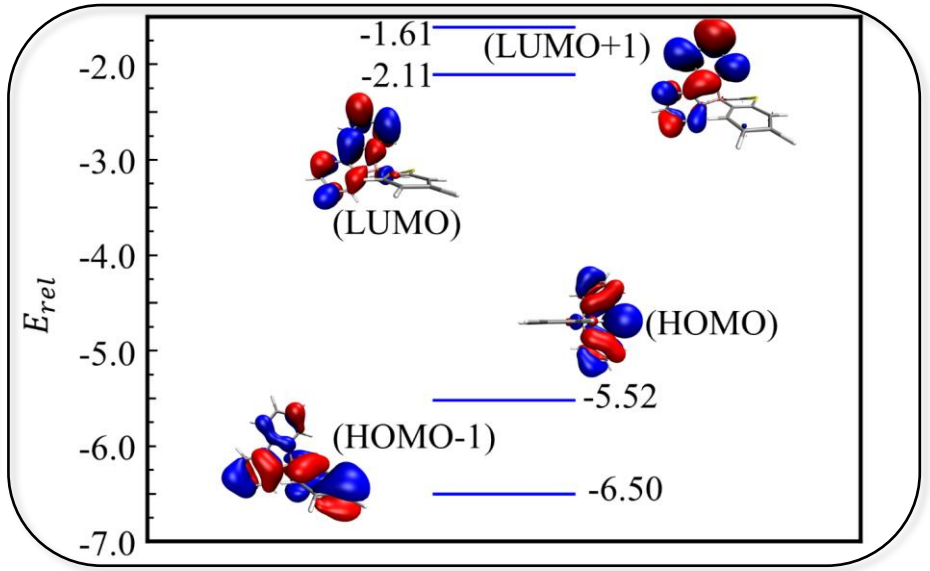
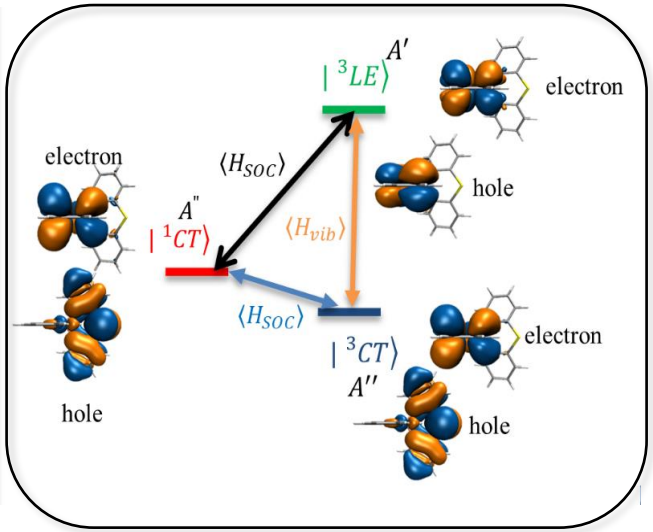
RESULTS AND DISCUSSIONS



Spiro-complex
Point group: C_s



No overlap between **HOMO-LUMO**
Lower ΔE_{ST} but **SOCME also low**



SOCME between S_1 and T_1: 0.078 cm^{-1}
SOCME between S_1 and T_2: 1.452 cm^{-1}

$$[T_1] \xrightarrow{k_{rISC}} [S_1] \xrightarrow{k_{ISC}} [T_1]$$

So, S_1 state population at time t is given by the following expression,

$$[S_1] = [T_1]_0 - \frac{[T_1]_0}{(k_{rISC}+k_{ISC})}\left(k_{ISC} + k_{rISC} \times e^{-(k_{ISC}+k_{rISC})t}\right)$$

Reorganization energy (λ_M)	k_{ISC}	k_{rISC}
λ_M= 0.3 eV	2.45×10^5 s^{-1}	9.70×10^4 s^{-1}
λ_M= 0.4 eV	8.12×10^4 s^{-1}	3.21×10^4 s^{-1}

$[T_1]_0$ = 100.0 as the initial population, we get, $[S_1]$ = 0.0003 after 100 ps

Non-radiative decay from nth Singlet state to mth Triplet state due to ISC can be calculated using Fermi-Golden rule

$$k_{ISC}^{nm} = \frac{2\pi}{\hbar}\rho_{FC}\left|\langle S_n|\widehat{H_{SO}}|T_m\rangle\right|^2$$

RESULTS AND DISCUSSIONS

Quantum dynamics simulation: Spin-Vibronic Coupling Hamiltonian

$$\begin{pmatrix} E_{T1}(Q_0) + \sum_i \frac{\omega_i}{2}\partial^2_{Q_i} + \frac{\omega_i}{2}Q_i^2 + \frac{\gamma^{T1}{}_i}{2}Q_i^2 + \frac{\varepsilon^{T1}{}_i}{24}Q_i^4 & E_{SOC}{}^{S1T1} & \sum_i \lambda_i Q_i \\ E_{SOC}{}^{S1T1} & E_{S1}(Q_0) + \sum_i \frac{\omega_i}{2}\partial^2_{Q_i} + \frac{\omega_i}{2}Q_i^2 + \frac{\gamma^{S1}{}_i}{2}Q_i^2 + \frac{\varepsilon^{S1}{}_i}{24}Q_i^4 & E_{SOC}{}^{S1T2} \\ \sum_i \lambda_i Q_i & E_{SOC}{}^{S1T2} & E_{T2}(Q_0) + \sum_i \frac{\omega_i}{2}\partial^2_{Q_i} + \frac{\omega_i}{2}Q_i^2 + \frac{\gamma^{T2}{}_i}{2}Q_i^2 + \frac{\varepsilon^{T2}{}_i}{24}Q_i^4 \end{pmatrix}$$

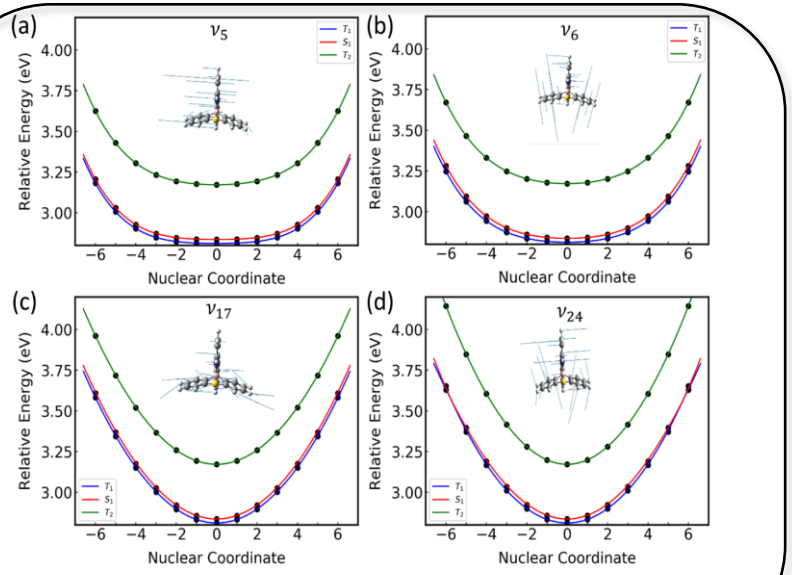
$$H_{nn} = E_n(Q_0) + \sum_i \frac{\omega_i}{2}\partial^2_{Q_i} + \frac{\omega_i}{2}Q_i^2 + \frac{\gamma^n{}_i}{2}Q_i^2 + \frac{\varepsilon^n{}_i}{24}Q_i^4$$

$$H_{nm} = \sum_i \lambda_i{}^{nm} Q_i$$

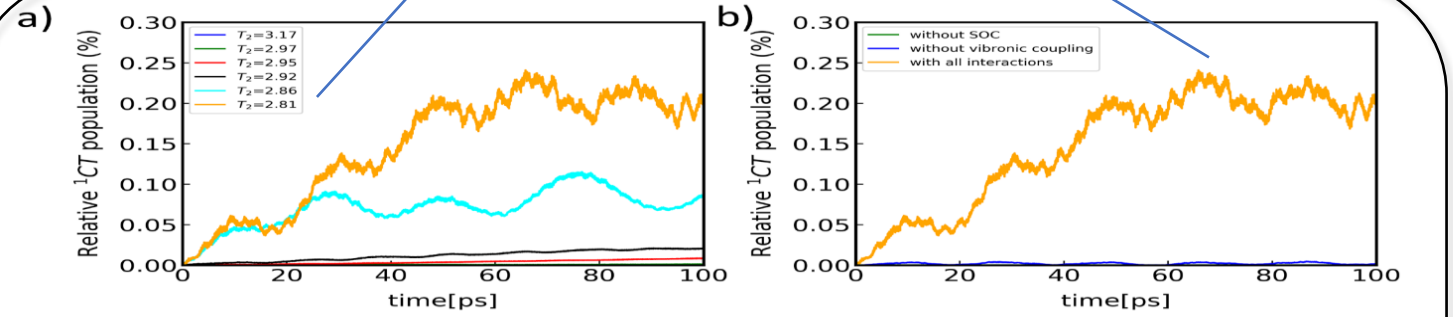
$$\lambda_i{}^{nm} = \sqrt{\frac{1}{8}\frac{\partial^2}{\partial Q_i^2}[V_m(Q) - V_n(Q)]^2}$$

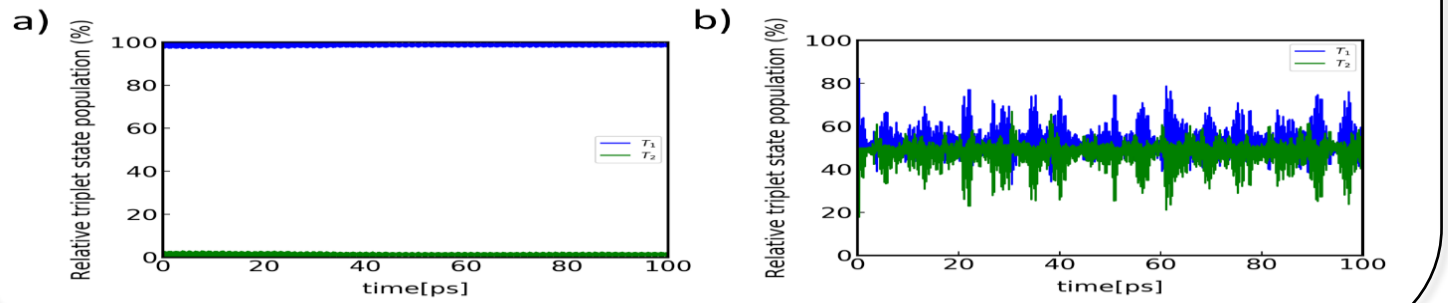
- We modelled this Hamiltonian to do excited state dynamics
- Inter state vibronic coupling (λ) parameters are calculated from potential energy scan
- Only low energy vibrations are taken into account

- When both the triplet states have same energy
- At that energy level both SOCME and vibronic coupling are opeartive



Low frequency vibrations





CONCLUSIONS

- Spiro arrangement of D-A system leads to CT nature in both S_1 and T_1 transitions
- SOCME between these two states is 0.078 cm^{-1}
- T_2 is LE in nature and it helps in rISC through spin-vibronic coupling (2^{nd} order perturbation)
- Apart from ΔE_{ST}, ΔE_{TT} gap is also playing a bigger role in rISC

COMPUTATIONAL METHODOLOGY

- Excited State energy potential scan were performed using B3LYP functional with 6-31+g(d,p) basis set using Gaussian 16 package.
- SCOME calculations were done using ZORA Hamiltonian with ADF2017 package using B3LYP functional and TZP basis set.
- Excited State dynamics were performed using MCTDH.

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THANK YOU