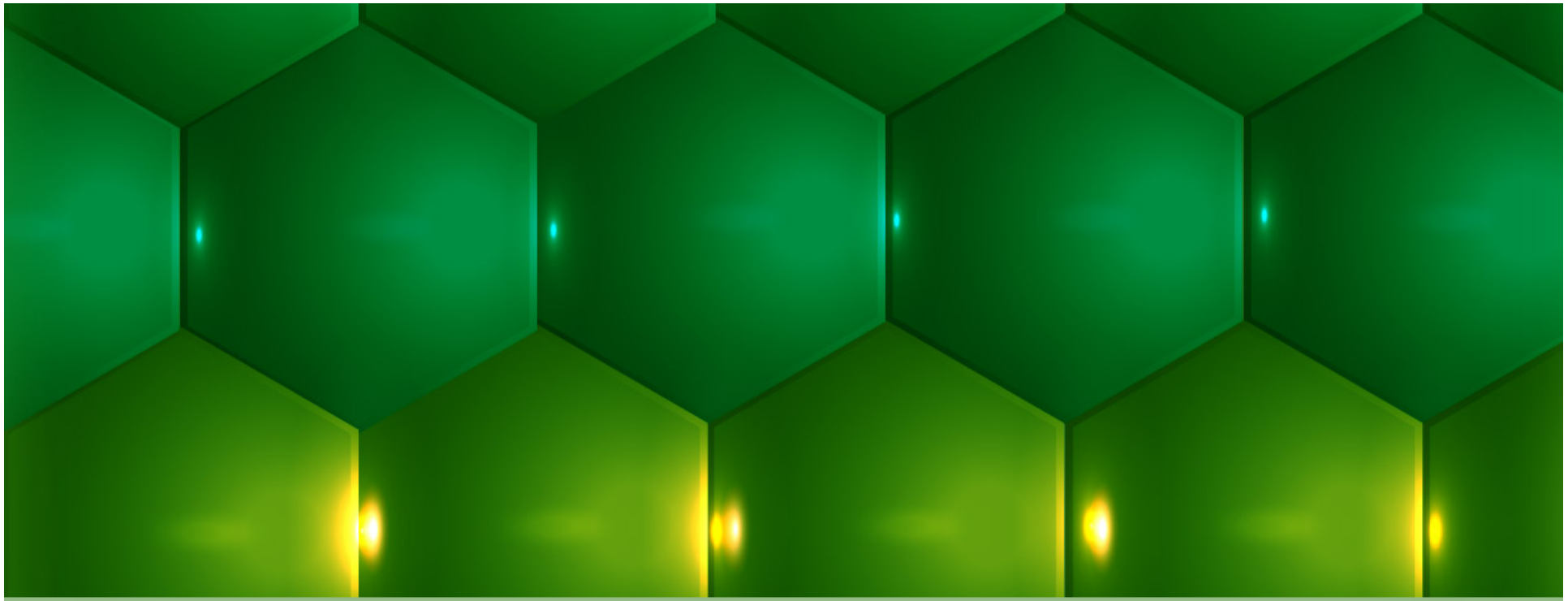

Singlet fission for solar energy conversion
A theoretical insight

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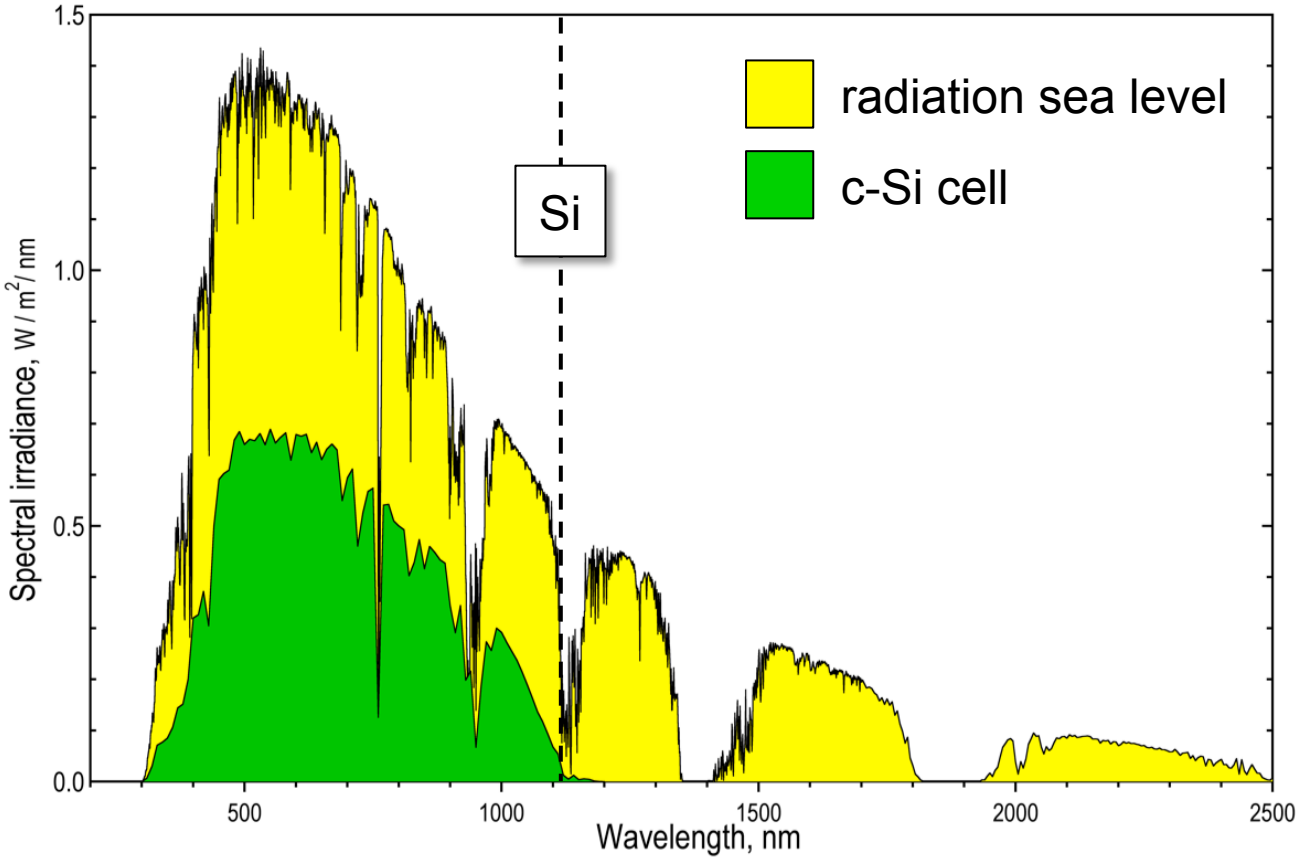
Euskal Herriko Unibertsitatea

Quantum Days in Bilbao

July 16, 2014

Harvesting Solar Energy

- Solar energy 1h = 1 year human consumption
- We use ~ 0.07% Earth radiation
- ~0.1% world's energy demand



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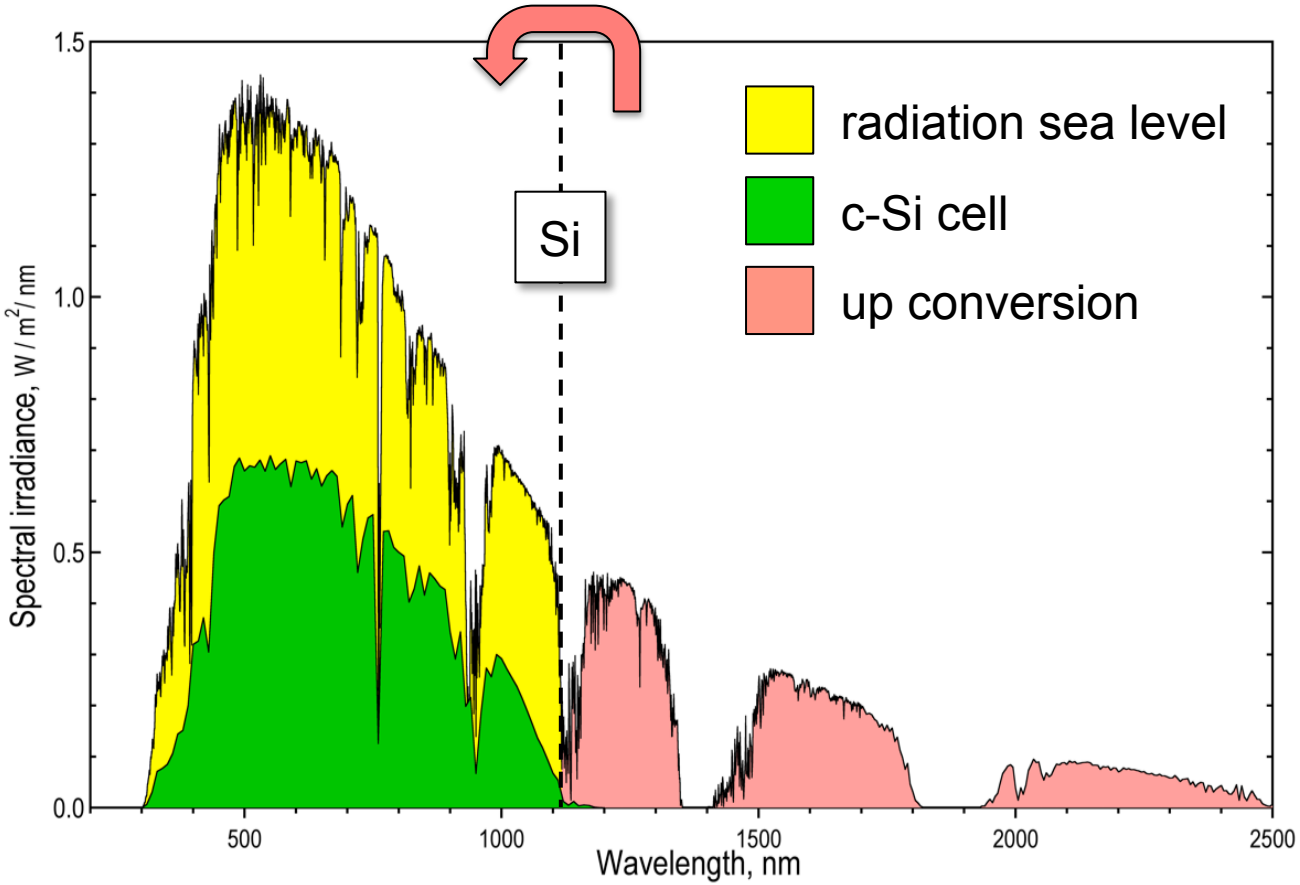
Up conversion

lanthanides ion pairs



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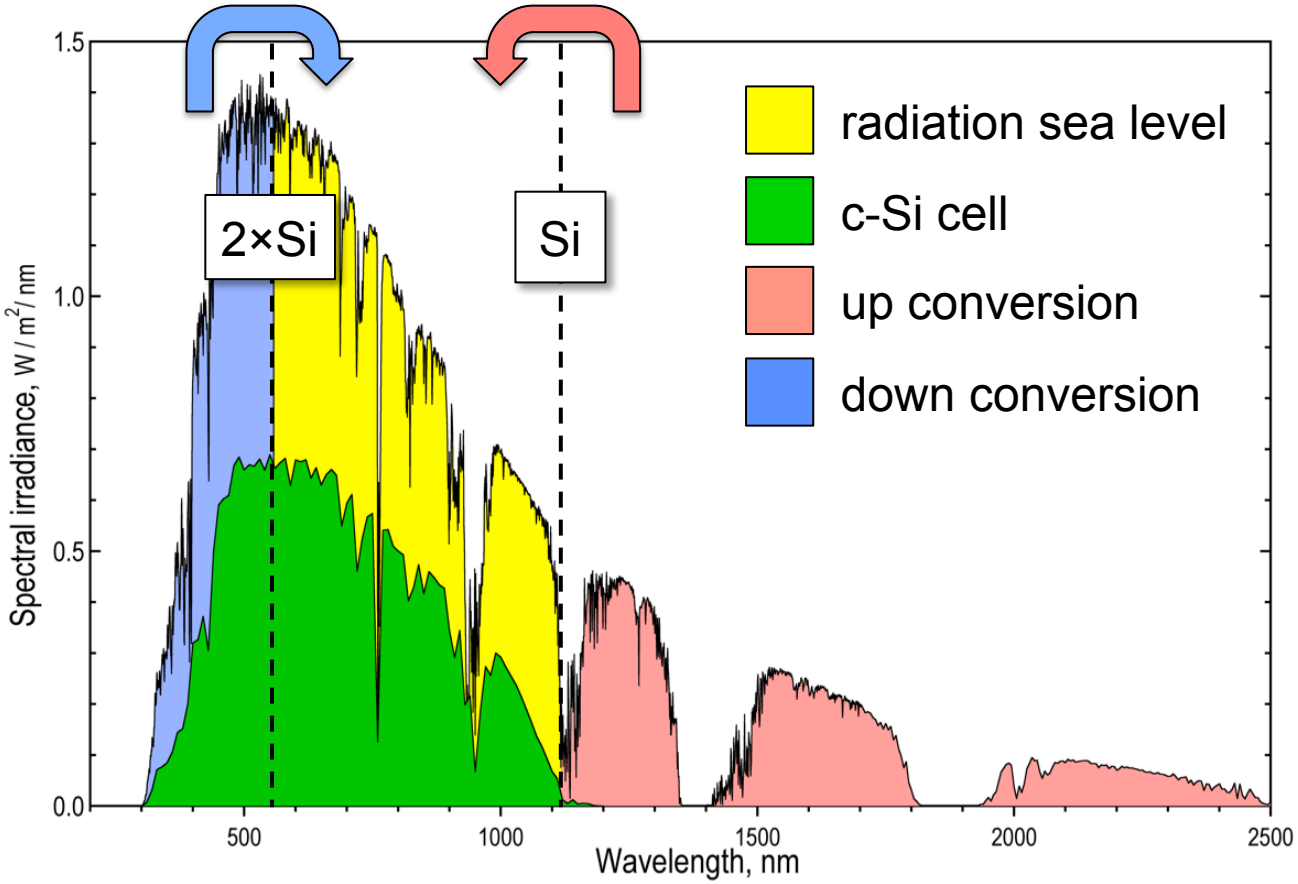


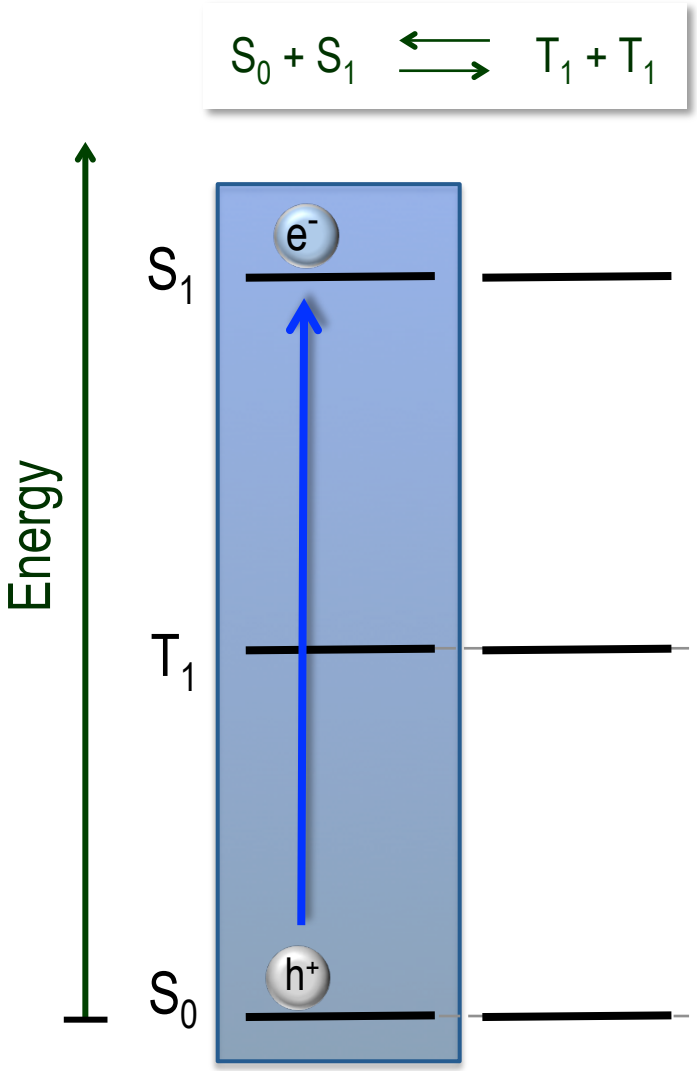
Up conversion

lanthanides ion pairs

Down conversion

- Quantum cutting
  rare earth glasses
- Multi Exciton Generation
  inorganic semiconductors
- Singlet Fission
  organic materials

Singlet Fission: definition



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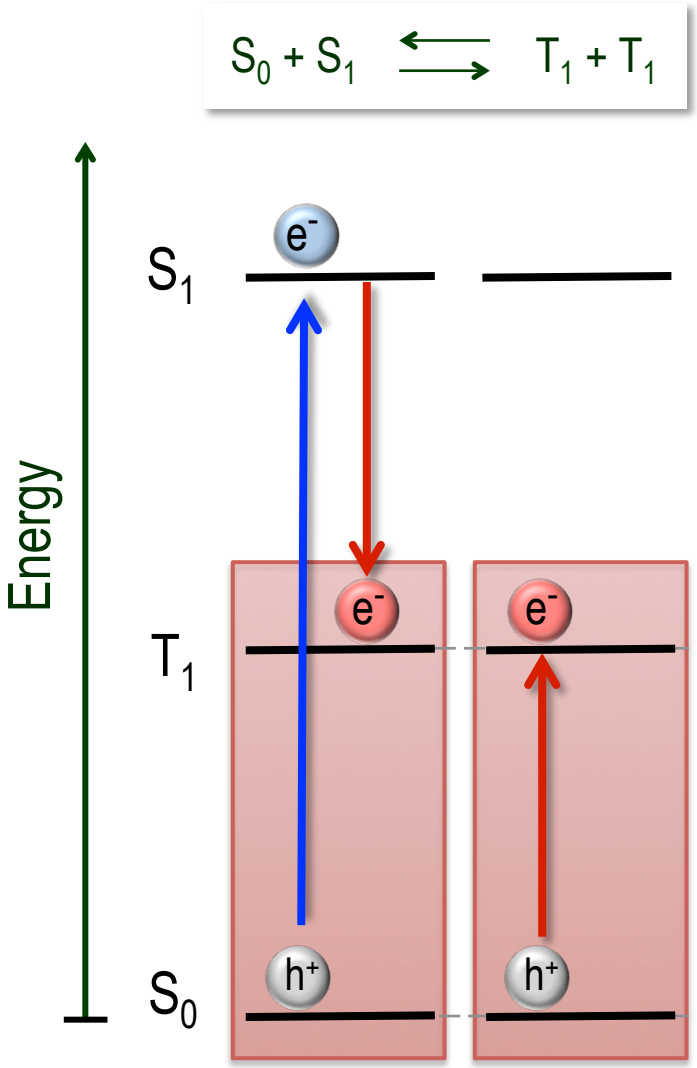

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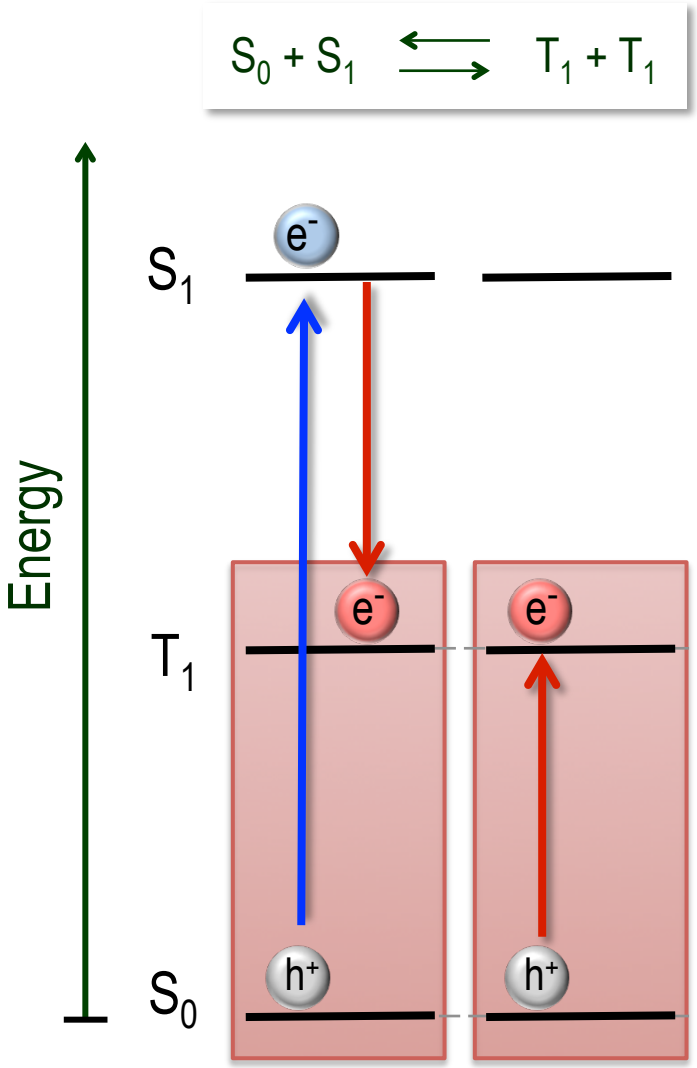

Properties

- organic compounds
- bimolecular process
- spin allowed
- very fast ≤ ps

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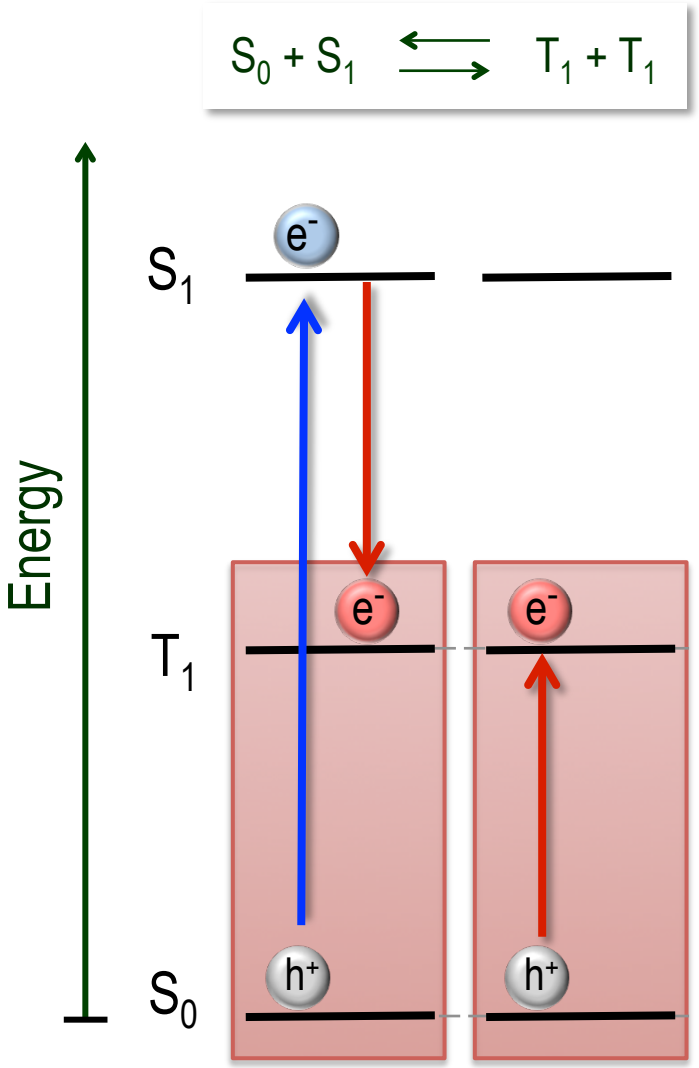

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- $E(S_1) \geq 2E(T_1)$
- $E(T_2) > 2E(T_1)$
- *proper* coupling

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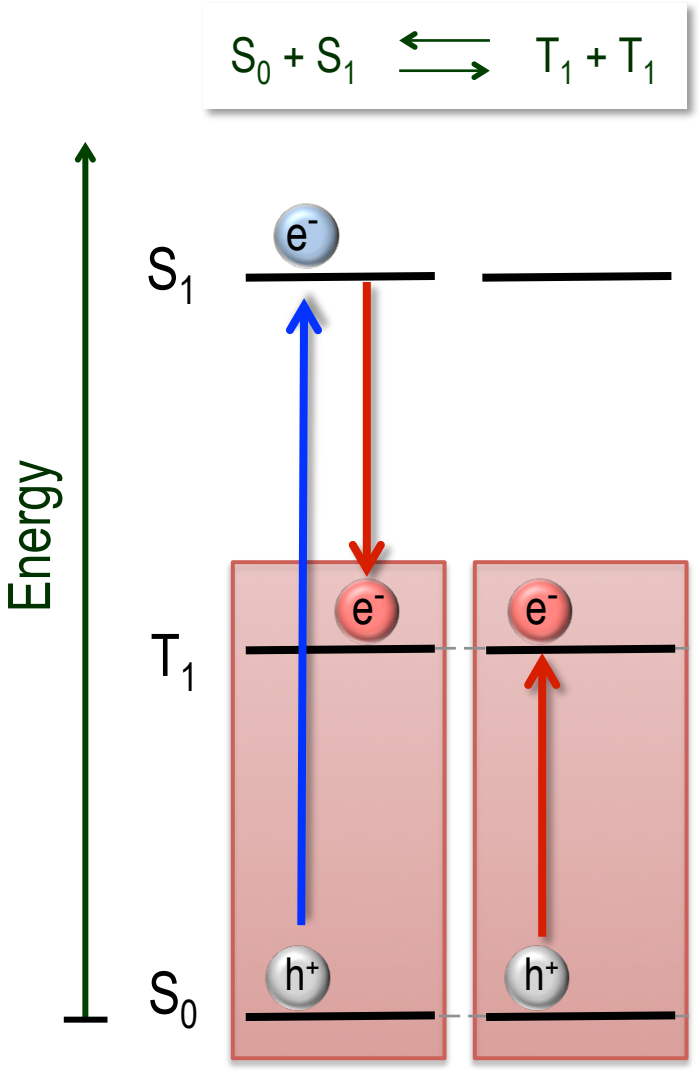

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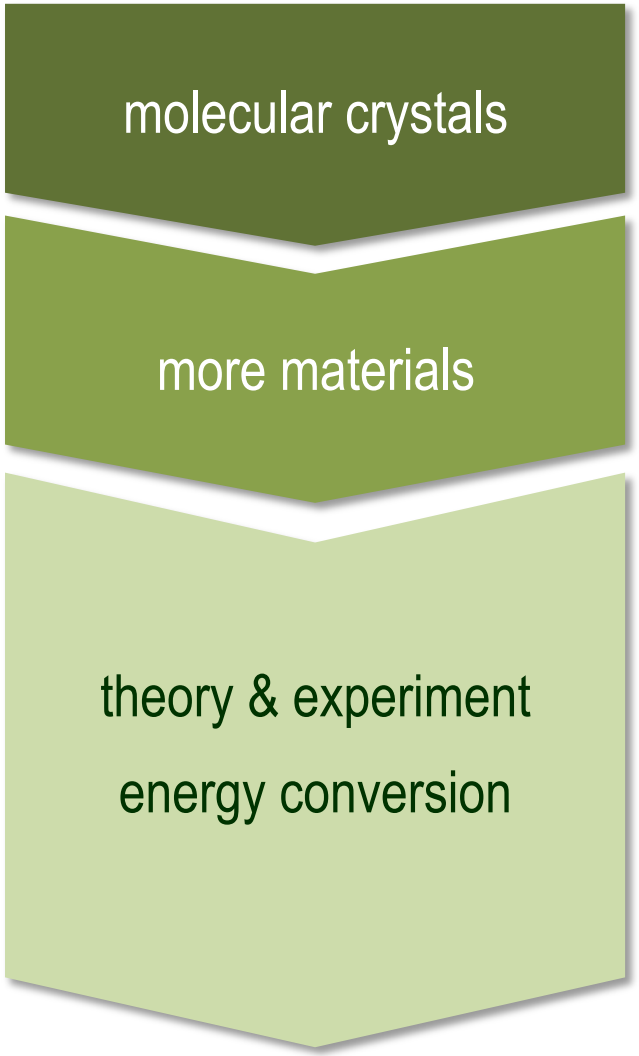
Detecting SF

- triplet generation > 100%
- delayed fluorescence
- magnetic field effects

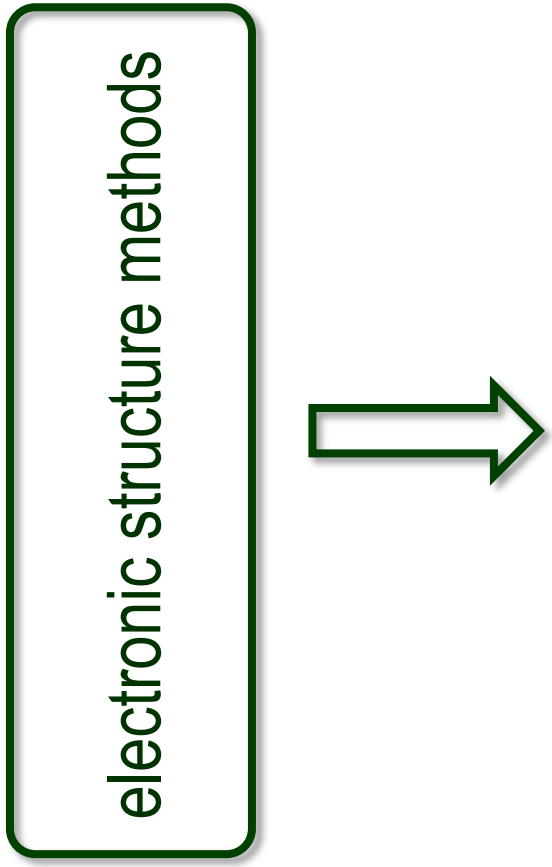
Singlet Fission: chronology

1965	photophysics of anthracene crystals
1968	low fluorescence in tetracene crystals
1980	carotenoids
1989	conjugated polymer
2004	proposed for photovoltaic applications
2006	theoretical guidelines
•	
•	new SF materials & development
•	
2013	SF in solar cells



Purpose: theory of SF

Computational characterization

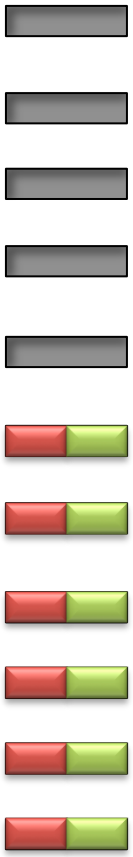


- States involved in SF
- Relative energies
- Mechanisms
- Rates of SF
- Key factors for SF
- Development of computational tools
- Propose/design new SF materials

Electronic states with RAS-SF

Restricted **A**ctive **S**pace **S**pin-**F**lip

Chemist's view



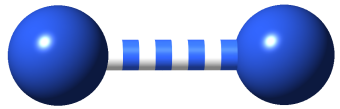
virtual orbitals

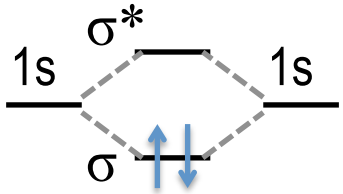
α spin

β spin

occupied orbitals

H_2 molecule





Electronic states with RAS-SF

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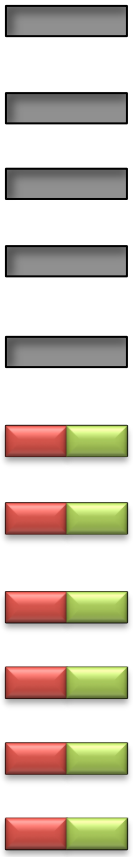

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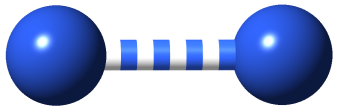

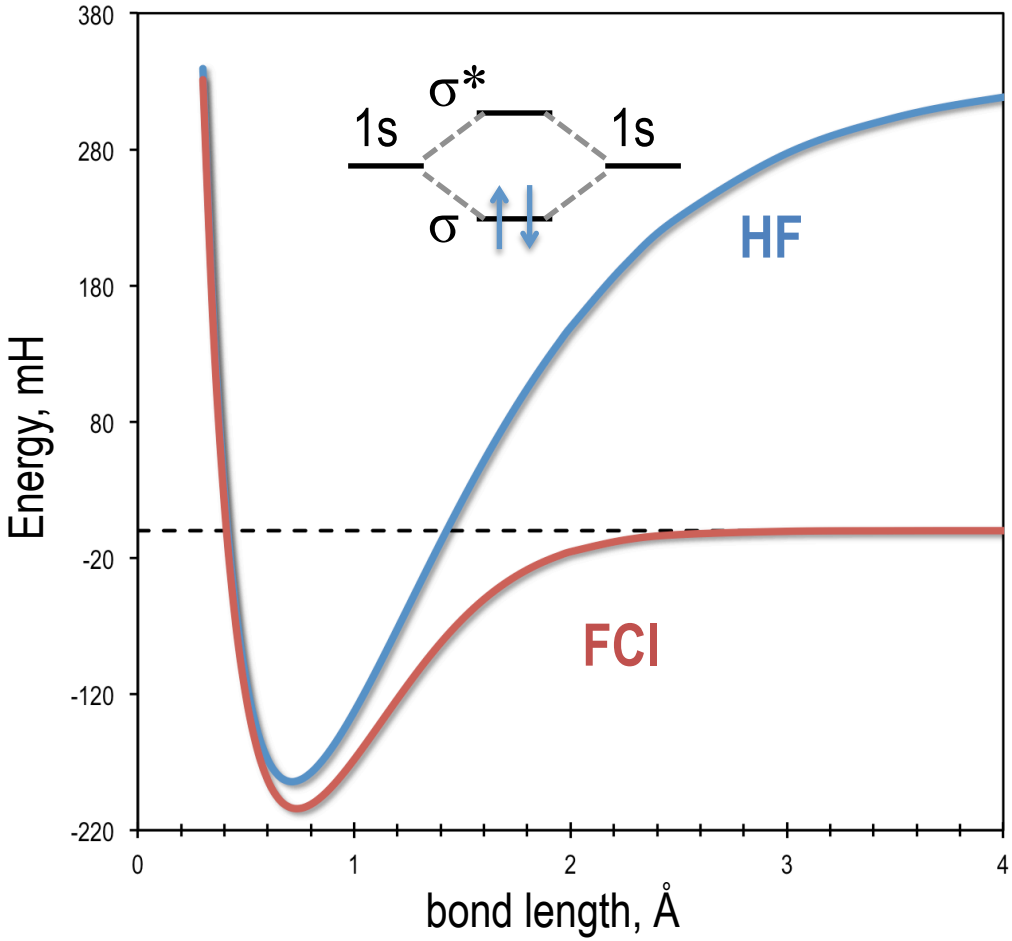

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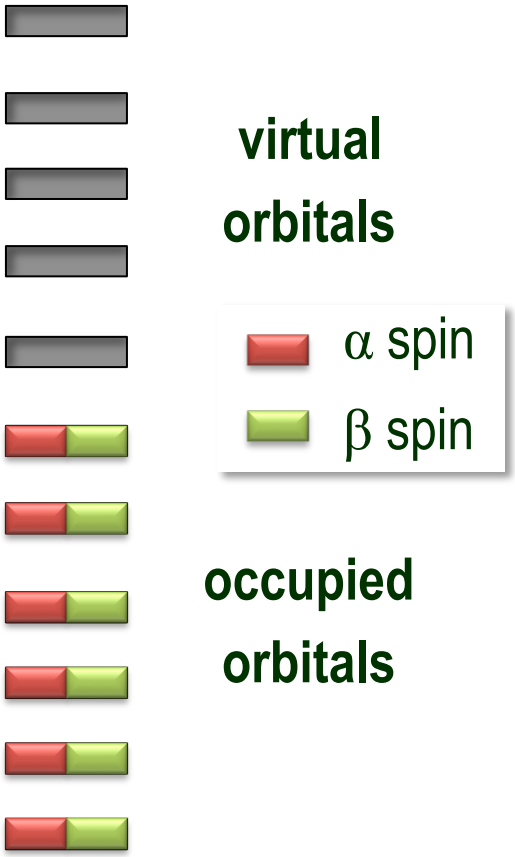

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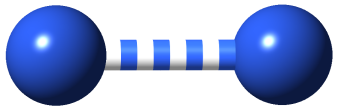
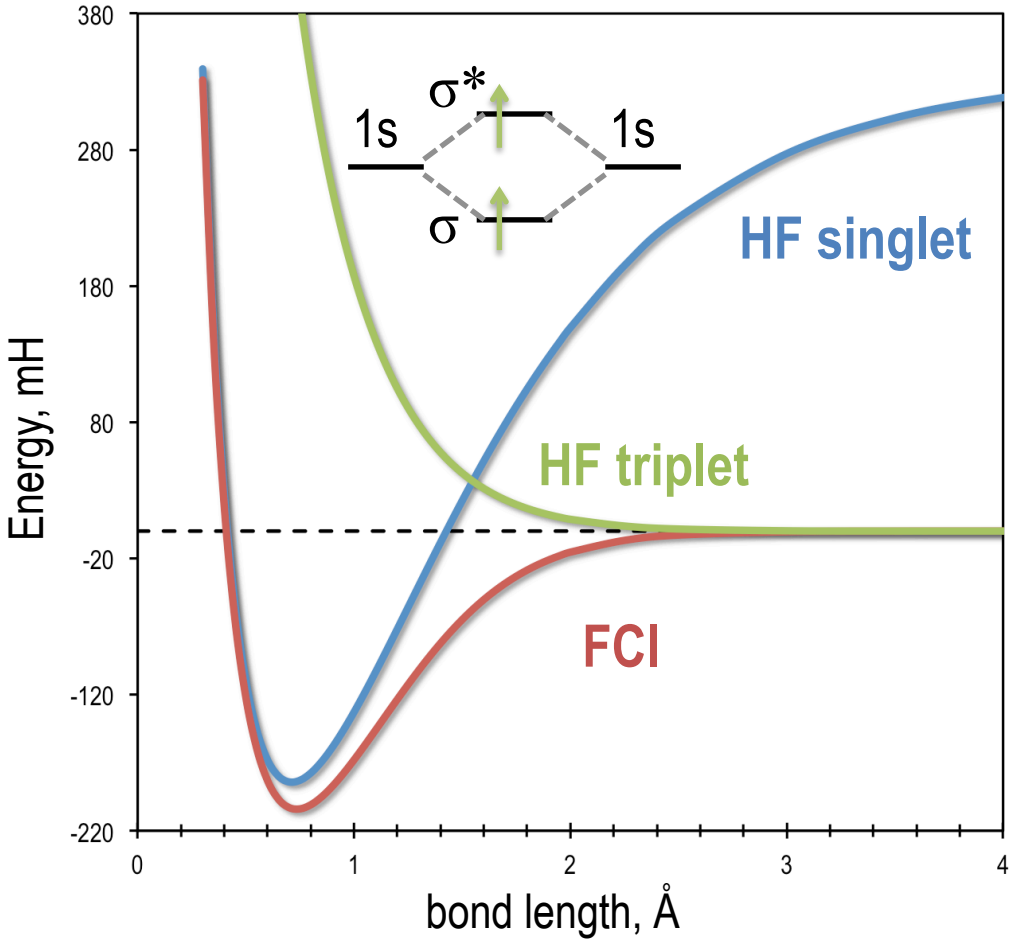
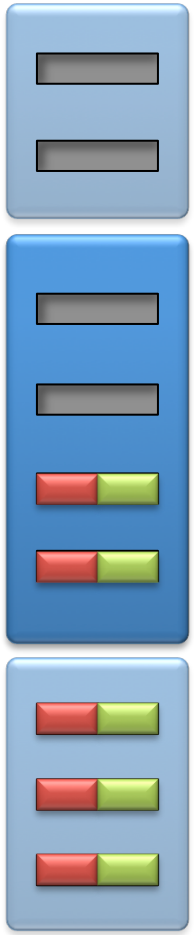




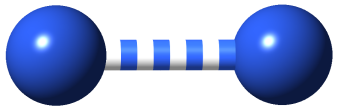
Electronic states with RAS-SF

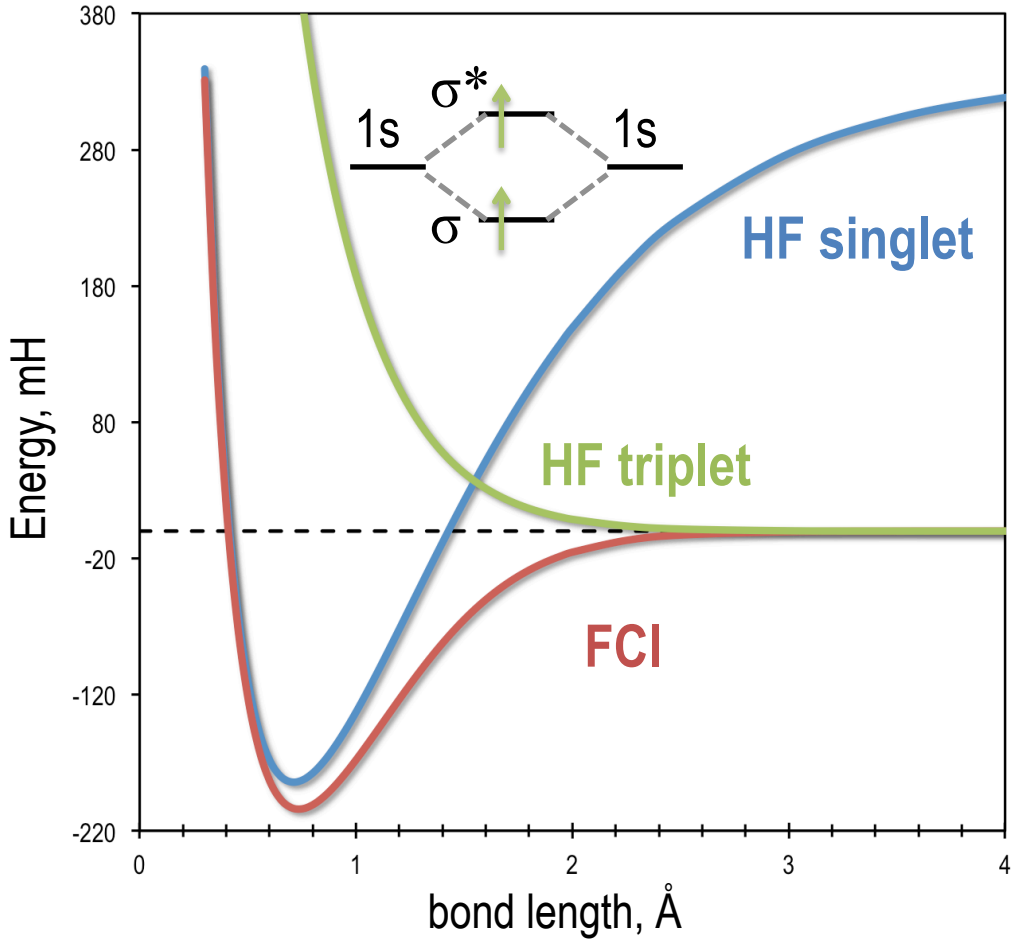
Restricted **A**ctive **S**pace **S**pin-**F**lip

Active Space



H_2 molecule

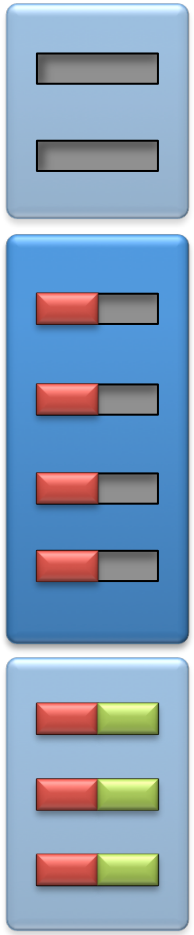




Electronic states with RAS-SF

Restricted **A**ctive **S**pace **S**pin-**F**lip

Active Space + High Spin

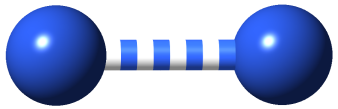


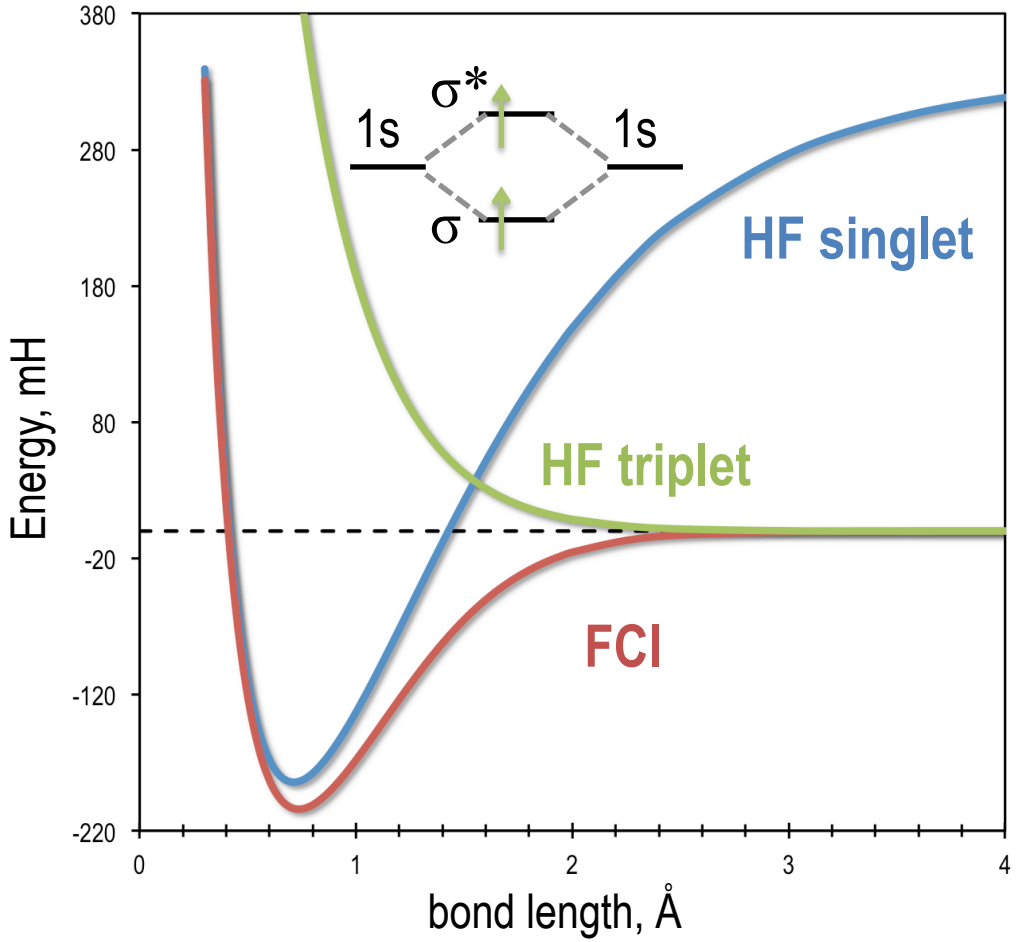
RAS3

RAS2

RAS1

H_2 molecule





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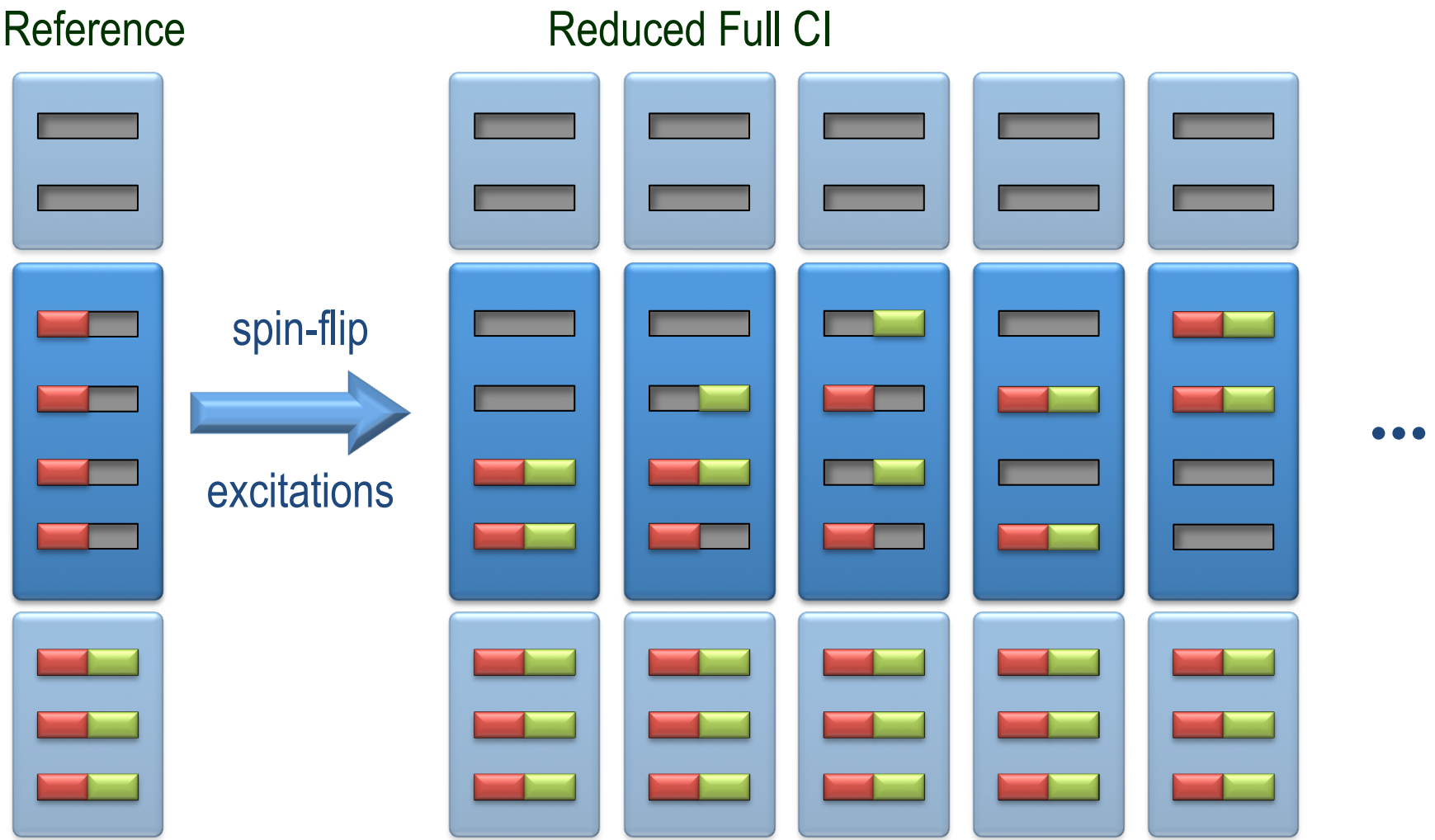
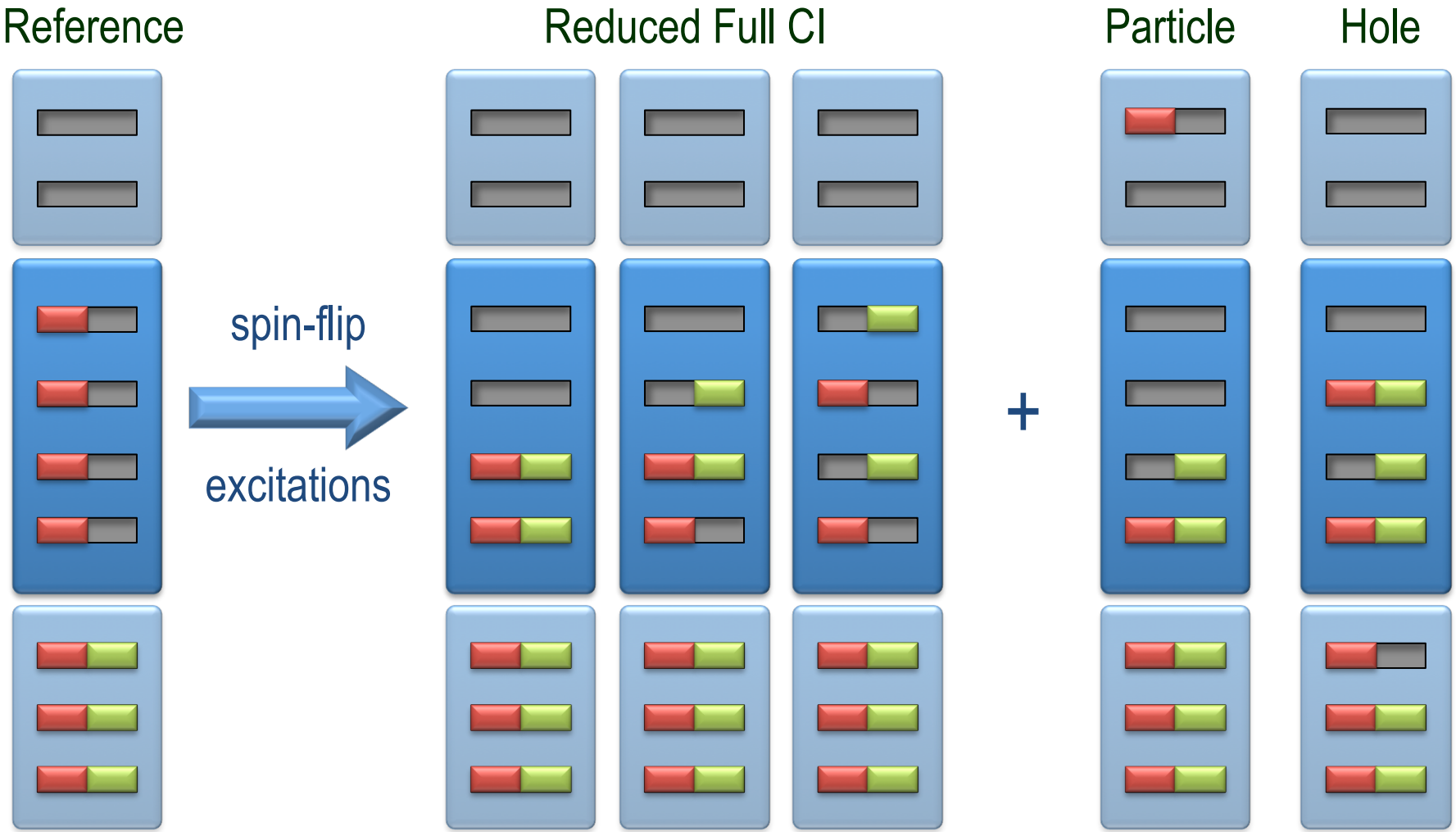


Electronic states with RAS-SF

Restricted **A**ctive **S**pace **S**pin-**F**lip

Casanova, Head-Gordon PCCP *10* **2009** 324
Casanova, JCP *137* **2012** 84105; JCC *34* **2013** 720



RAS-SF algorithms

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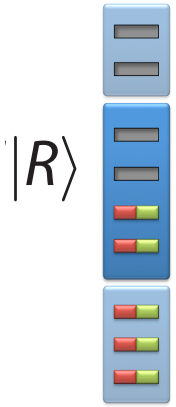

configuration	class	occupation	dimensions
$\|R\rangle$	active	**1010 | 1001**	$\binom{m}{n}\binom{m}{n}$
	hole	**h 1110 | 1001**	$2O\binom{m}{n+1}\binom{m}{n}$
	part	**p 1000 | 1001**	$2V\binom{m}{n-1}\binom{m}{n}$

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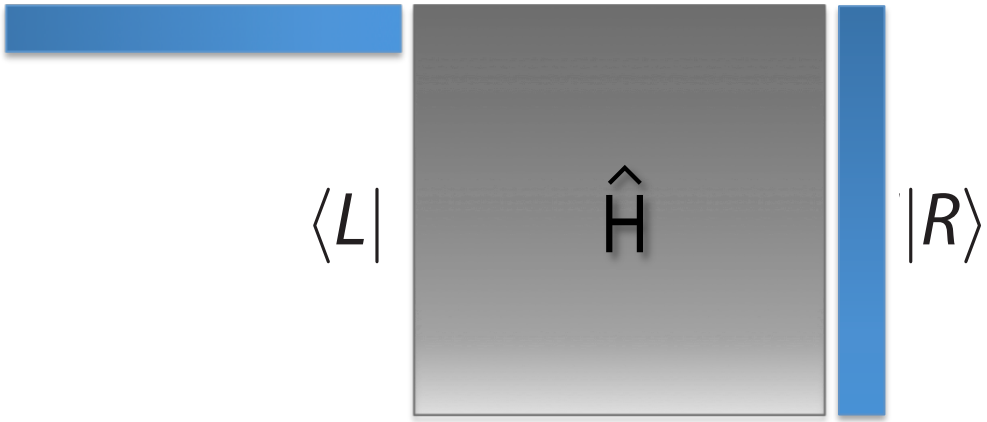

RAS-SF algorithms

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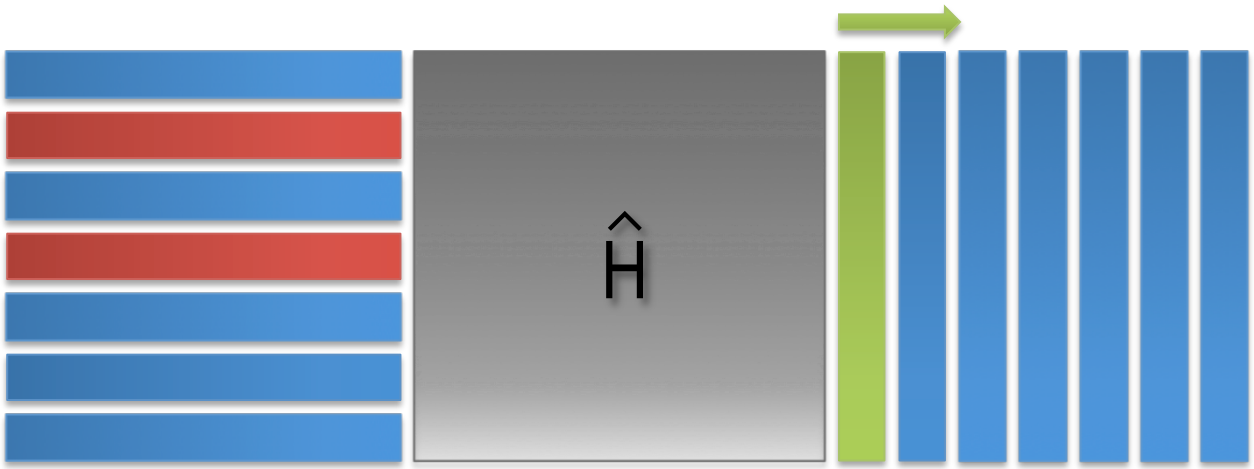

Algorithm

Configuration driven

TDDFT, CIS

RAS-SF algorithms

Restricted **A**ctive **S**pace **S**pin-**F**lip

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$$\sum_R \langle L|\hat{H}|R\rangle C_R = E\, C_L$$

$$\langle L|\hat{H}|R\rangle = \sum_{\mu\nu} A^{LR}_{\mu\nu}(\mu|\nu) + \sum_{\mu\nu\lambda\rho} B^{LR}_{\mu\nu\lambda\rho}(\mu\nu|\lambda\rho)$$

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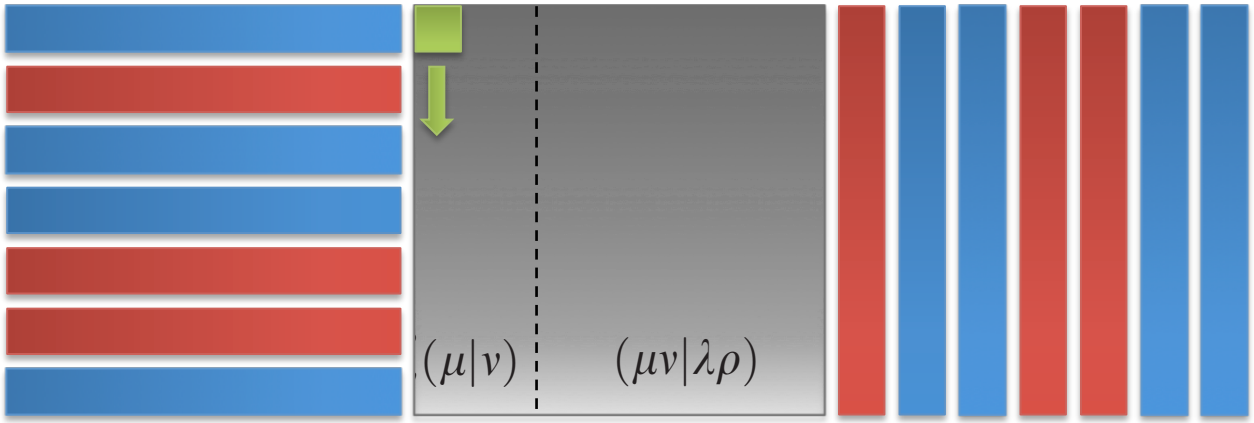


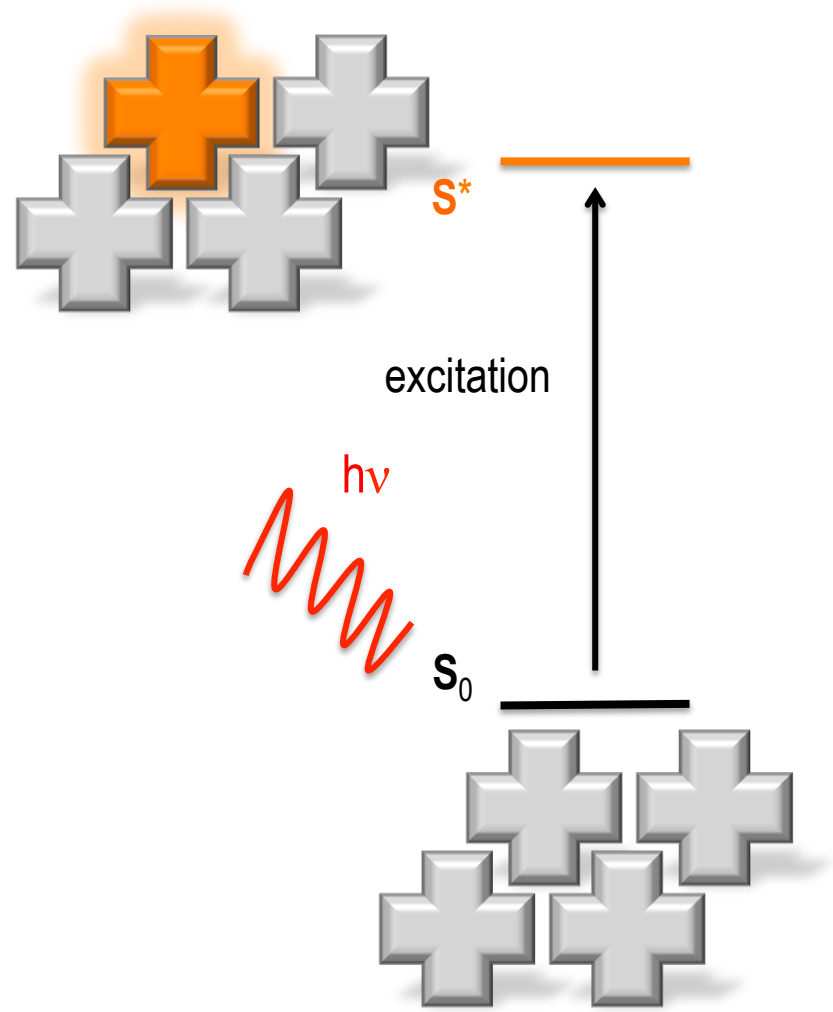
Algorithm

Integral driven

CAS, FCI

Singlet Fission: mechanism

$S_0 + S_1 \rightleftharpoons {}^1(TT) \rightleftharpoons T_1 + T_1$



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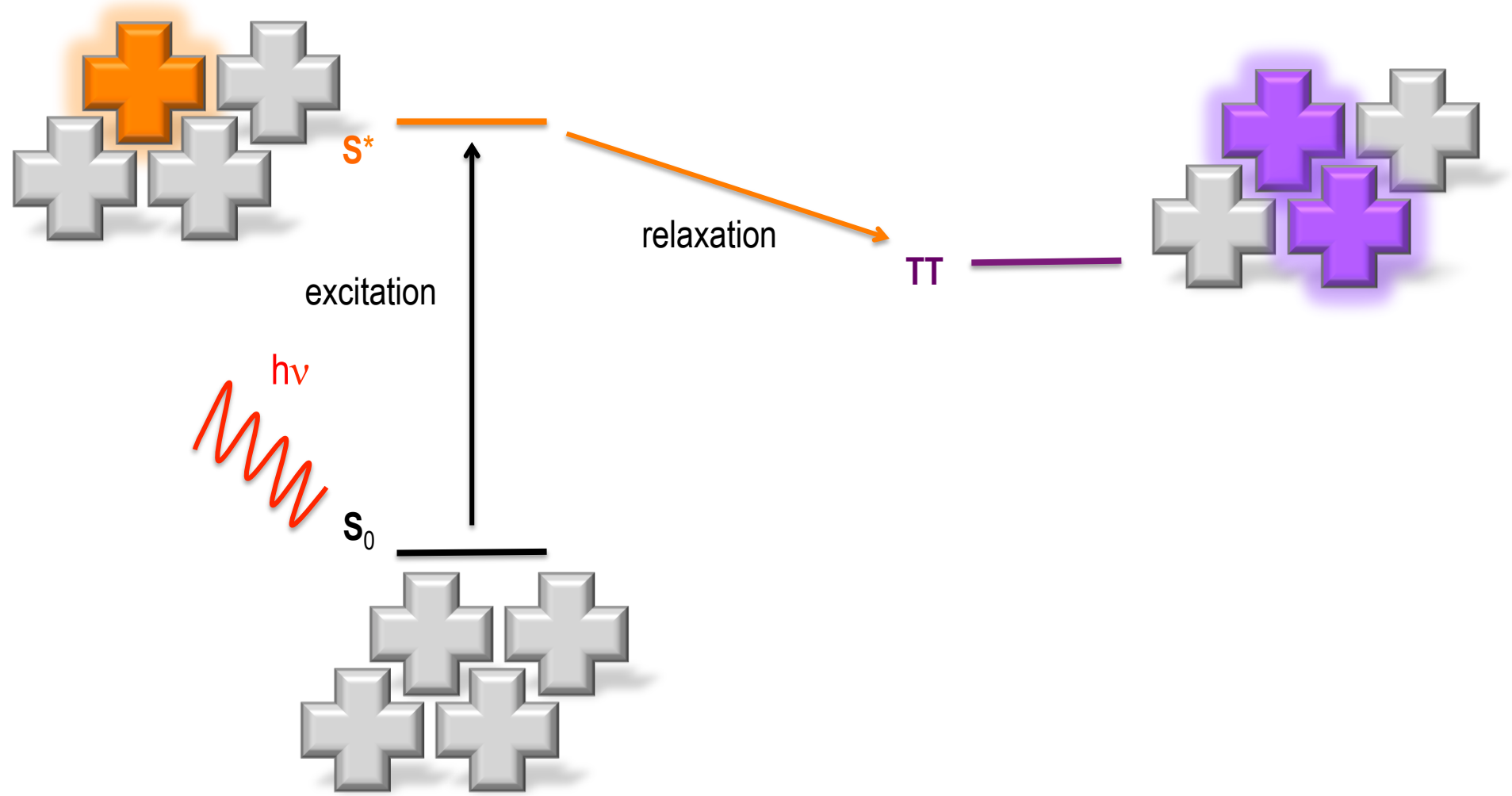

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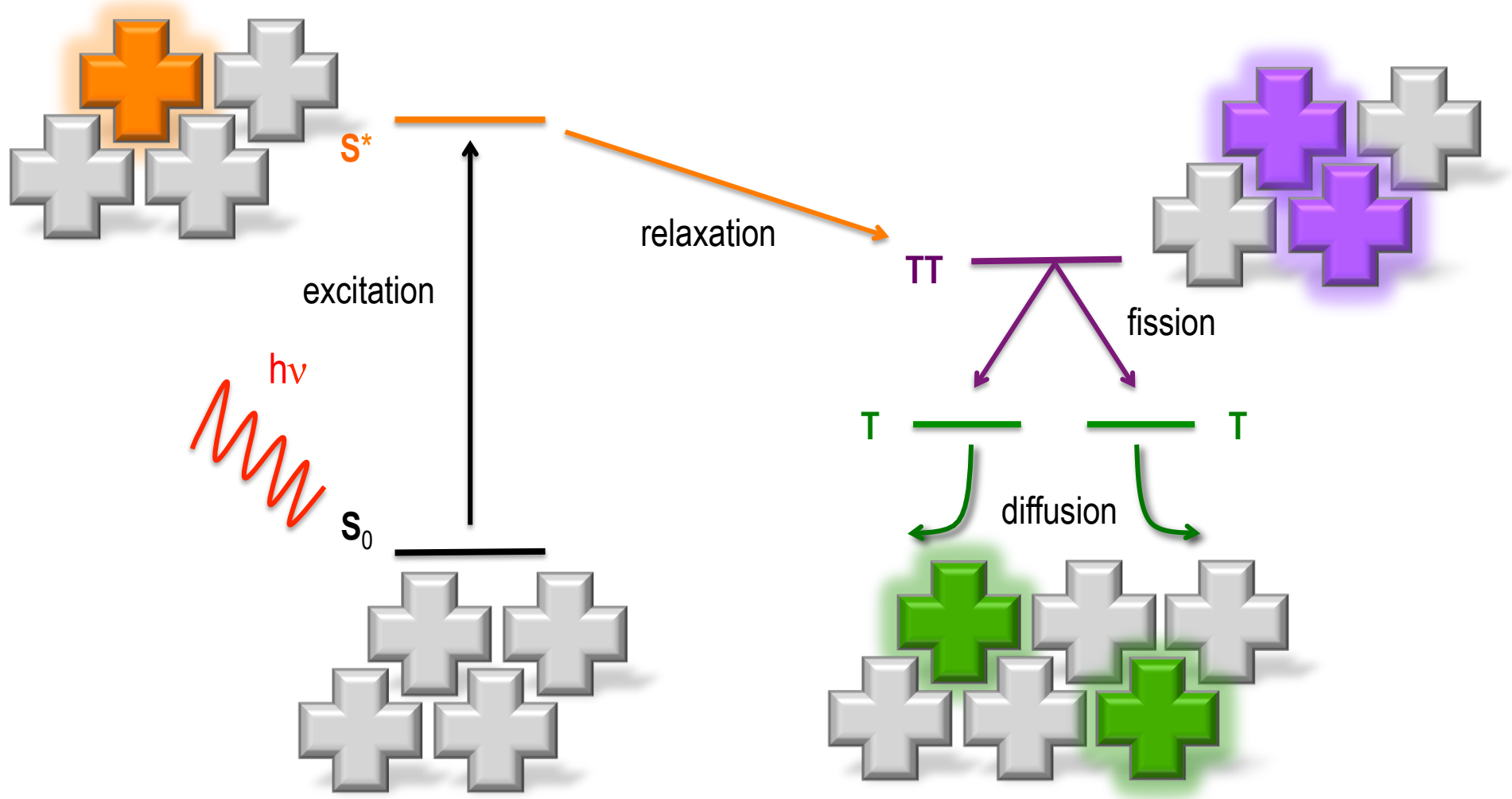

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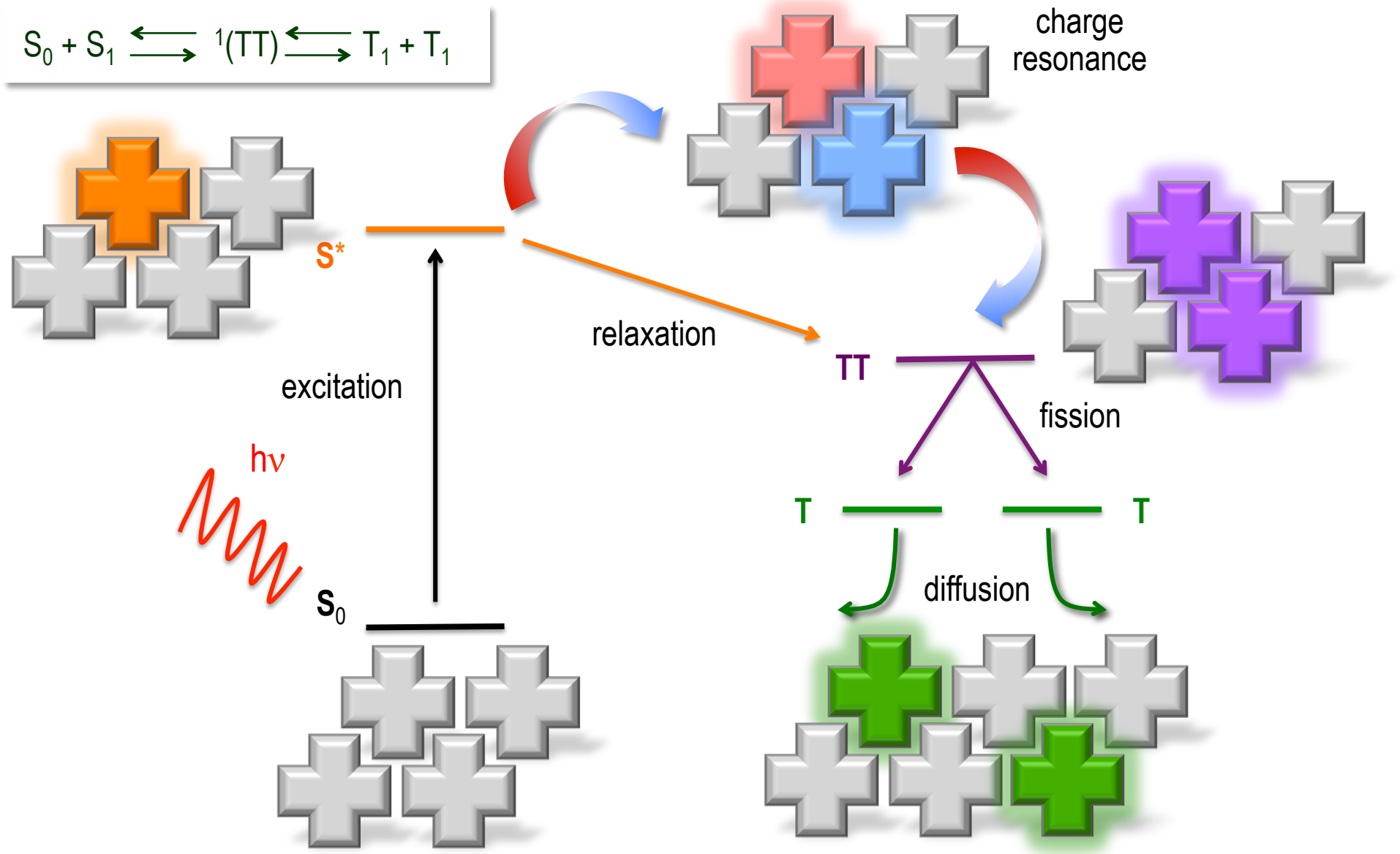


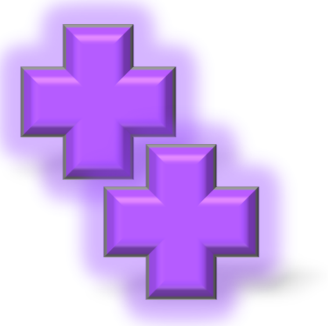
Singlet Fission: electronic states

SF precursor ^{1}**TT**

$$\hat{S}^2 \left| {}^1TT \right\rangle = s(s+1) \left| {}^1TT \right\rangle$$

$$^1\mathbf{TT} = \left[\uparrow\downarrow \; \uparrow\downarrow \right] + \left[\downarrow\uparrow \; \downarrow\uparrow \right] + {}^1/_2 \left[\downarrow\downarrow \; \uparrow\uparrow + \uparrow\uparrow \; \downarrow\downarrow + \uparrow\downarrow \; \uparrow\downarrow + \downarrow\uparrow \; \downarrow\uparrow \right]$$

T_1T_{-1} $T_{-1}T_1$ T_0T_0



Singlet Fission: electronic states

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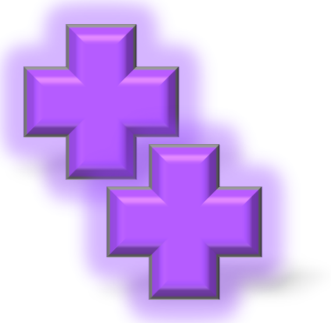
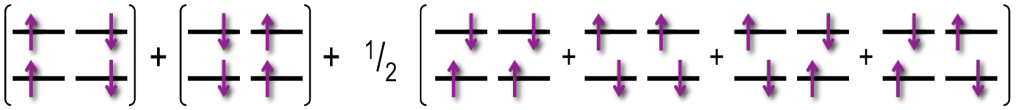
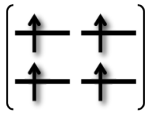


^{1}TT = 

T_1T_{-1} $T_{-1}T_1$ T_0T_0

Reference

^{5}TT



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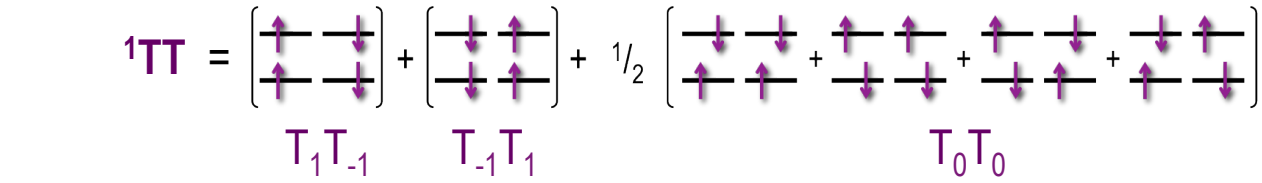
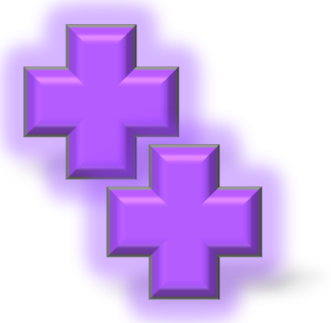
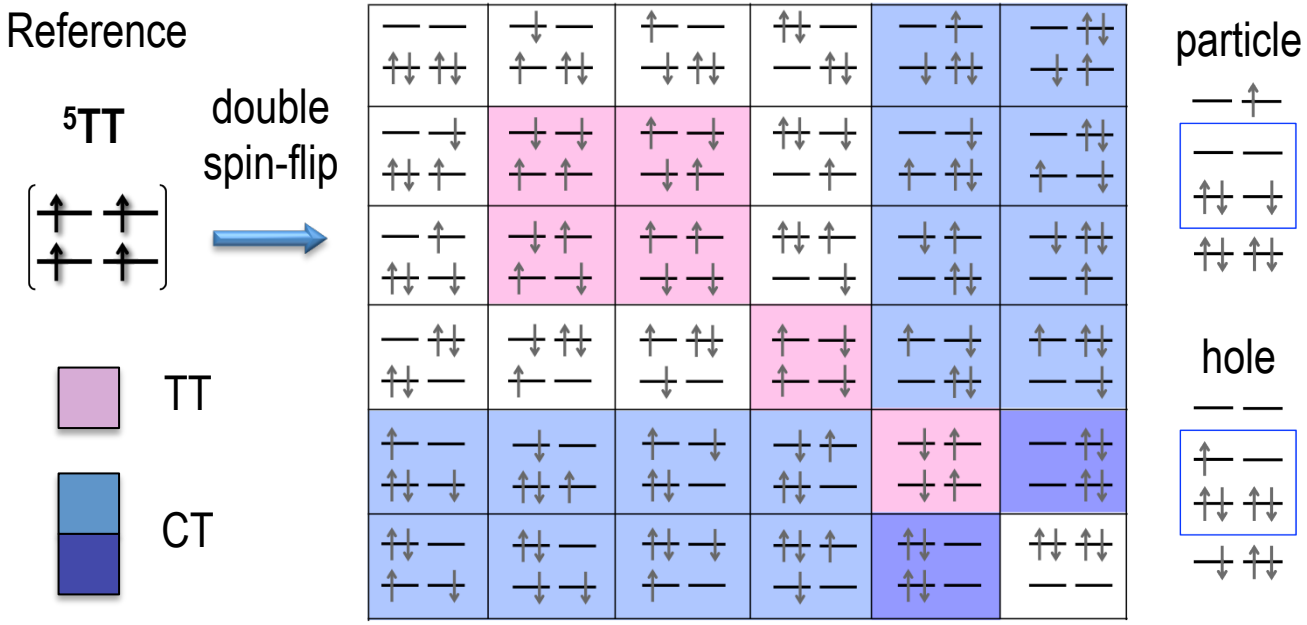






RAS-2SF wavefunction

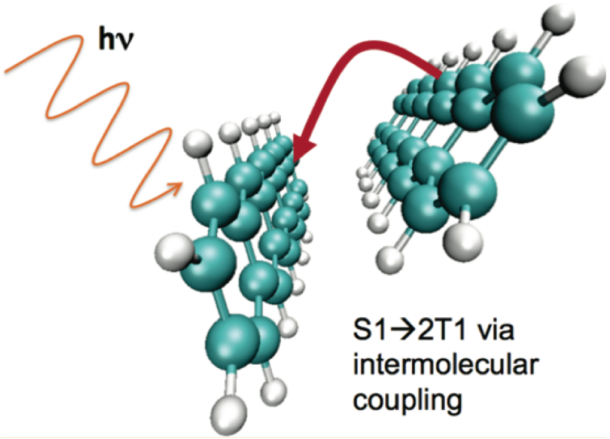
- single exciton
- multiple exciton
- charge transfer

Singlet Fission: molecular vibration

Intermolecular distortion

Phonon like

Chromophore coupling



tetracene, pentacene

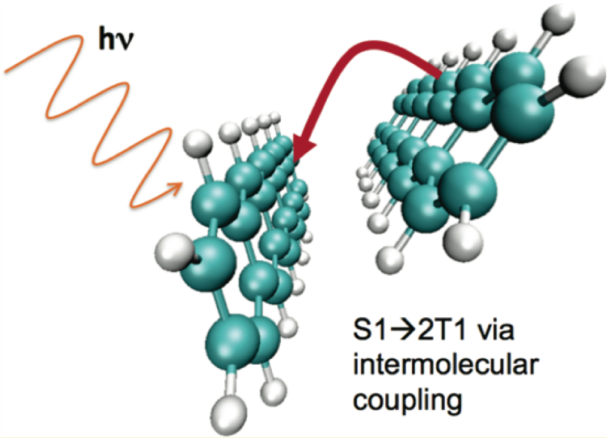
JACS, *133* **2011** 19944

Singlet Fission: molecular vibration

Intermolecular distortion

Phonon like

Chromophore coupling



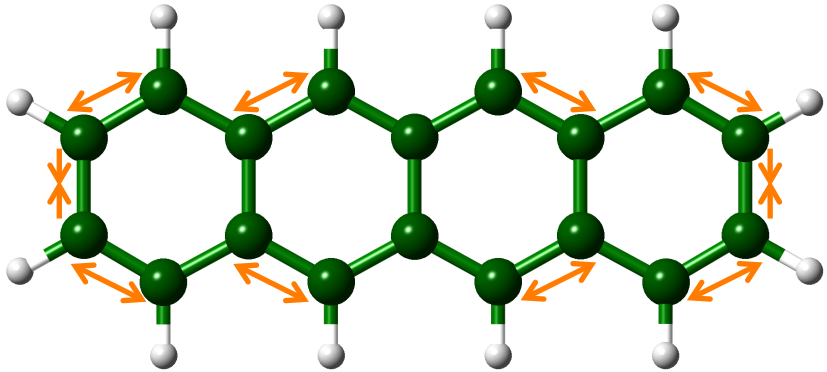
tetracene, pentacene

JACS, *133* **2011** 19944

Intramolecular distortion

S_1 optimization

Energy levels



a_g “breathing” mode

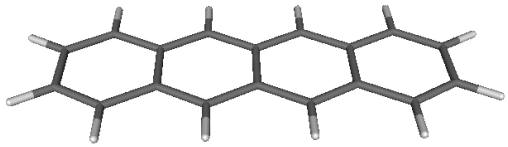
tetracene, DPT, rubrene

JCTC *10* **2014** 324

Singlet Fission: molecular vibration

Intramolecular distortion

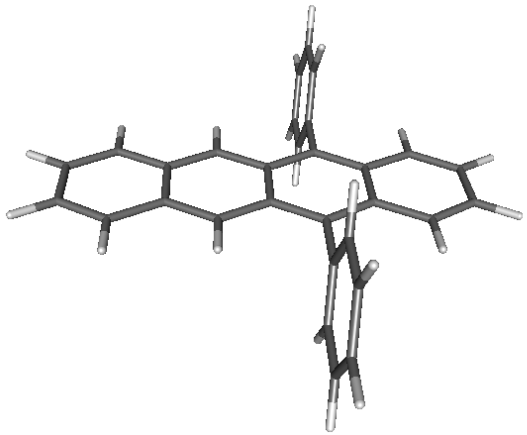
Tetracene



"SF thermally activated"

Jundt et al., CPL (1995)

DPT



"large thermodynamic driving force for SF"

Roberts et al., JACS (2012)

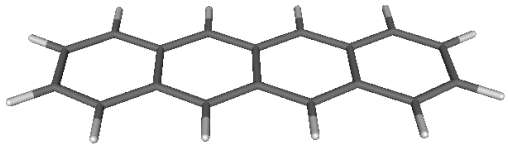
Singlet Fission: molecular vibration

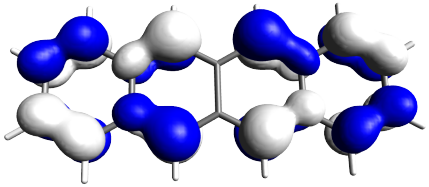
Intramolecular distortion

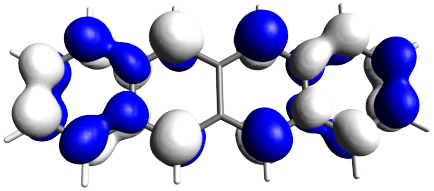
HOMO

LUMO

Tetracene







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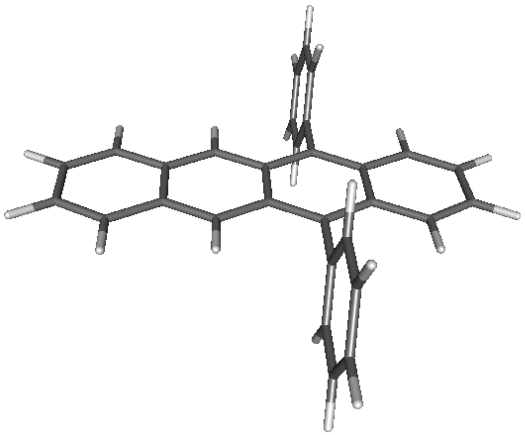
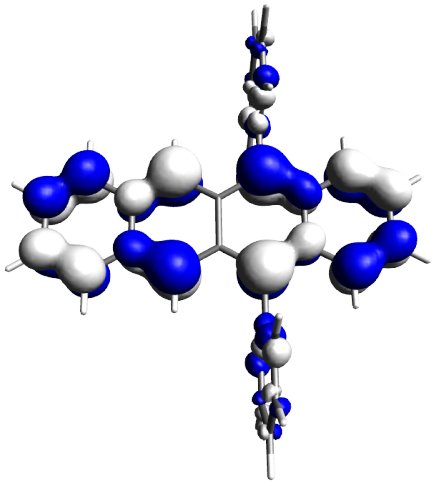
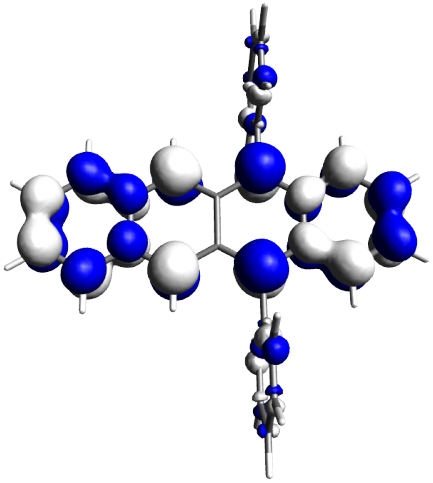


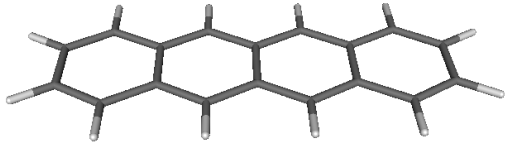




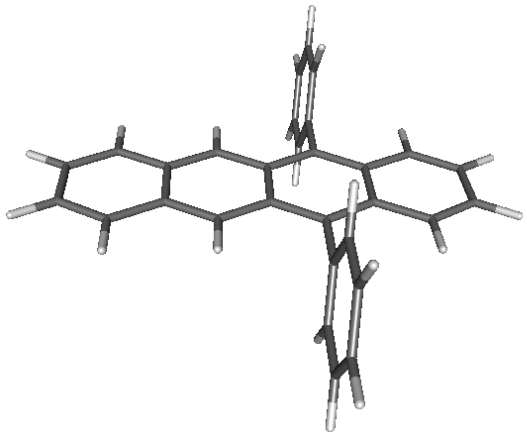
Singlet Fission: molecular vibration

Intramolecular distortion

Tetracene

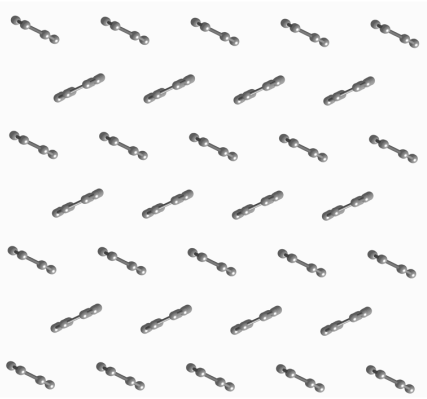


DPT



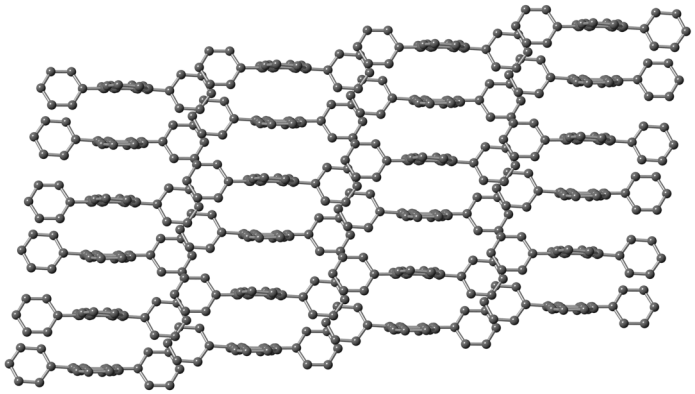
Crystal structure

herringbone lattice



Holmes et al., Chem. Eur. J. (1999)

slip-stack structure

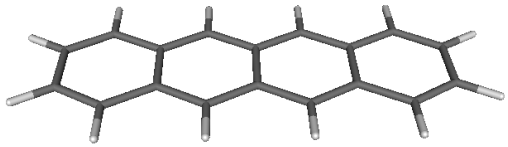


Roberts et al., JACS (2012)

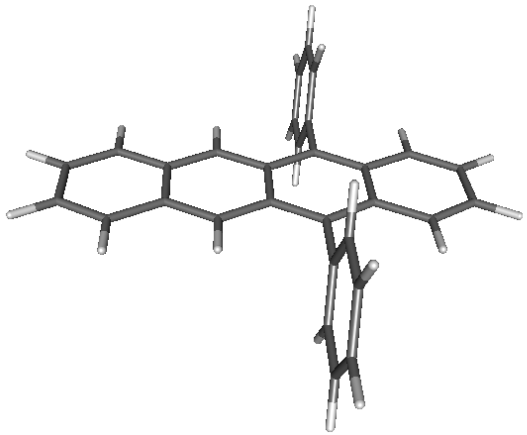
Singlet Fission: molecular vibration

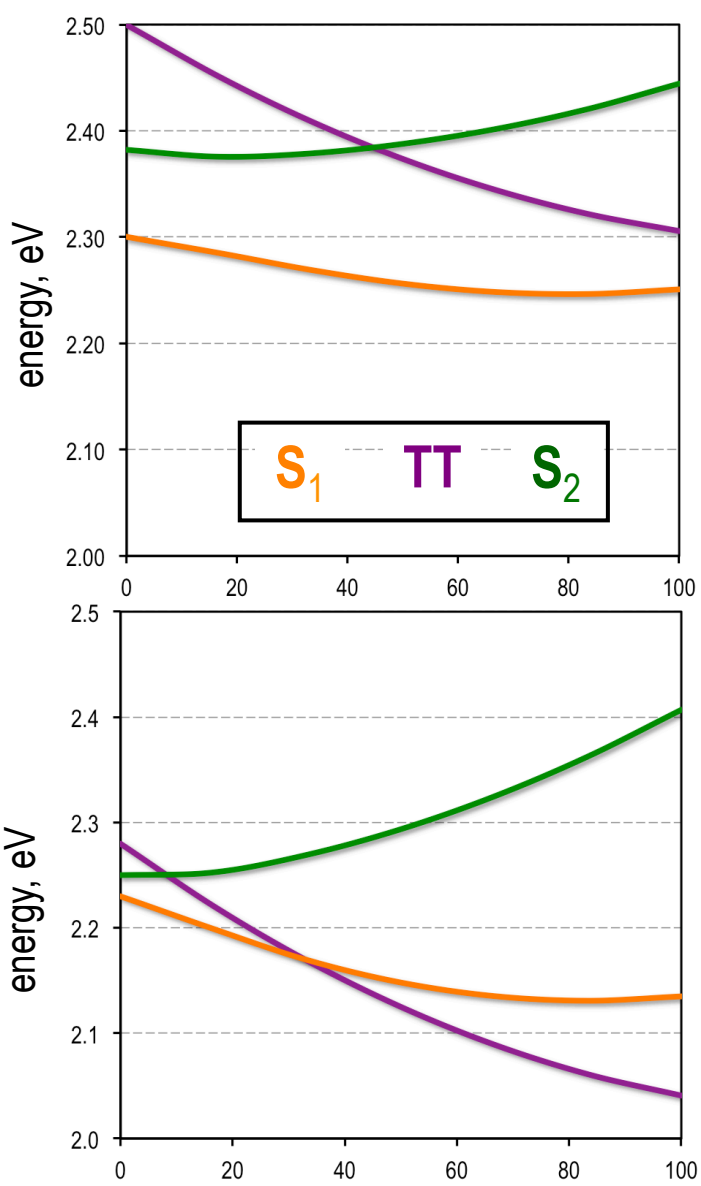
Intramolecular distortion

Tetracene



DPT

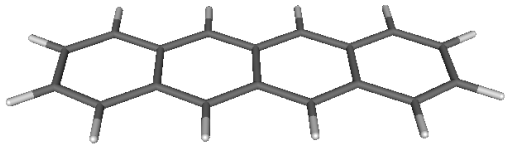




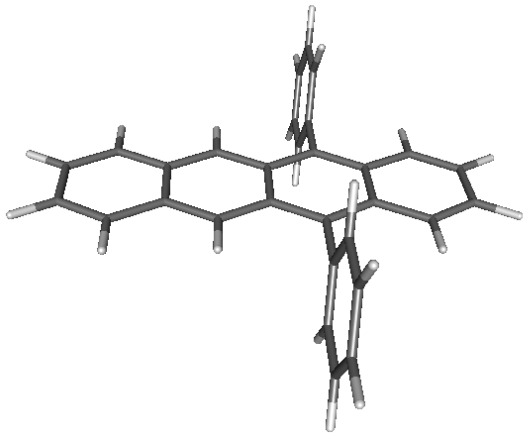
Singlet Fission: molecular vibration

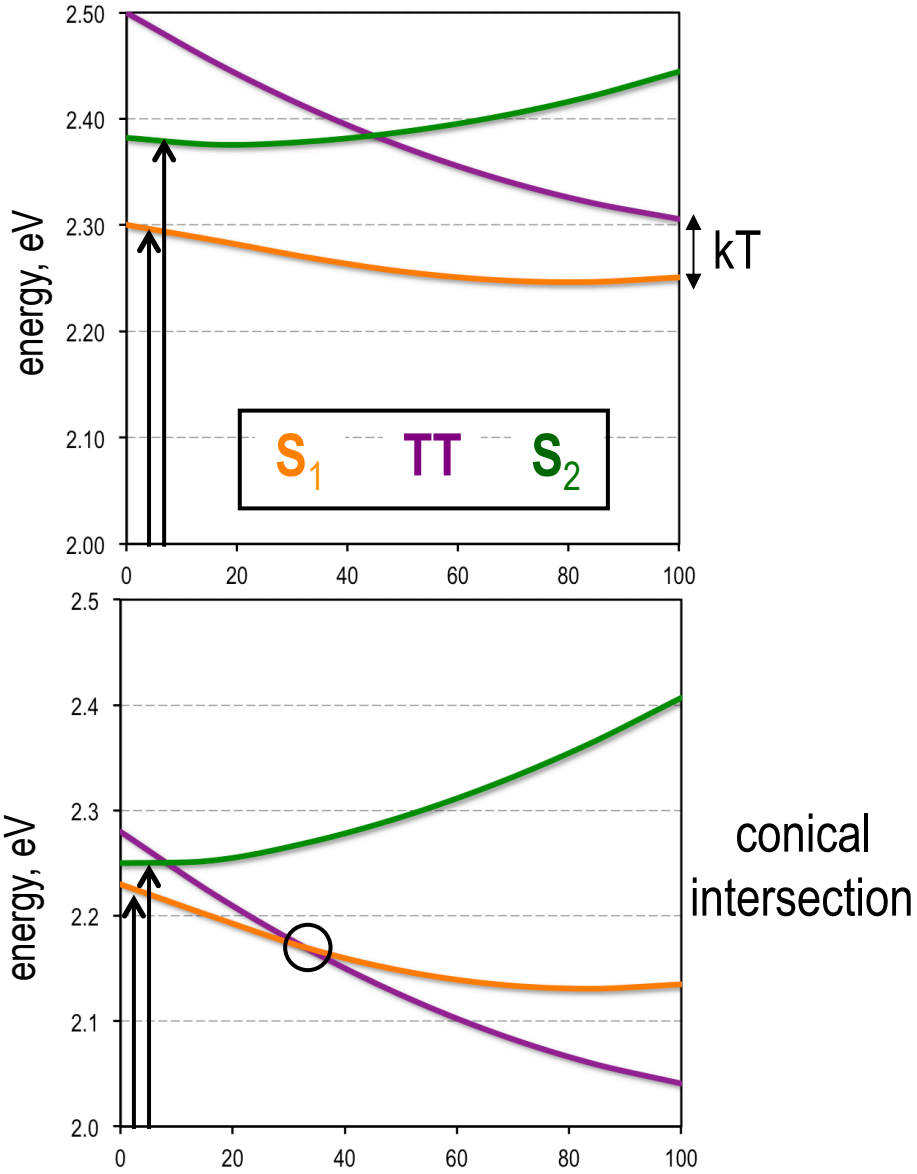
Intramolecular distortion

Tetracene



DPT





Singlet Fission: chromophore coupling

SF transition rate

$S_0S_1 \longrightarrow TT$

$$\omega(\mathrm{SF}) = \frac{2\pi}{\hbar} \left| \langle TT | \hat{H} | S_0 S_1 \rangle \right|^2 \rho[E]$$

Fermi golden rule

Singlet Fission: chromophore coupling

SF transition rate

$$\omega(\mathrm{SF}) = \frac{2\pi}{\hbar}\left|\langle TT|\hat{H}|S_0S_1\rangle\right|^2 \rho[E]$$

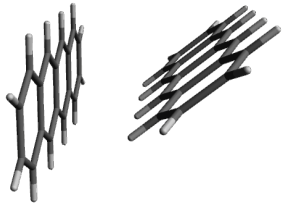
small

-2.2 meV

$S_0S_1 \longrightarrow TT$

Fermi golden rule

Tetracene dimer



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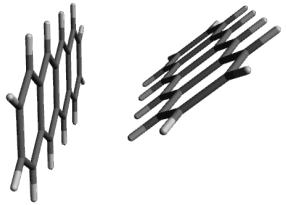
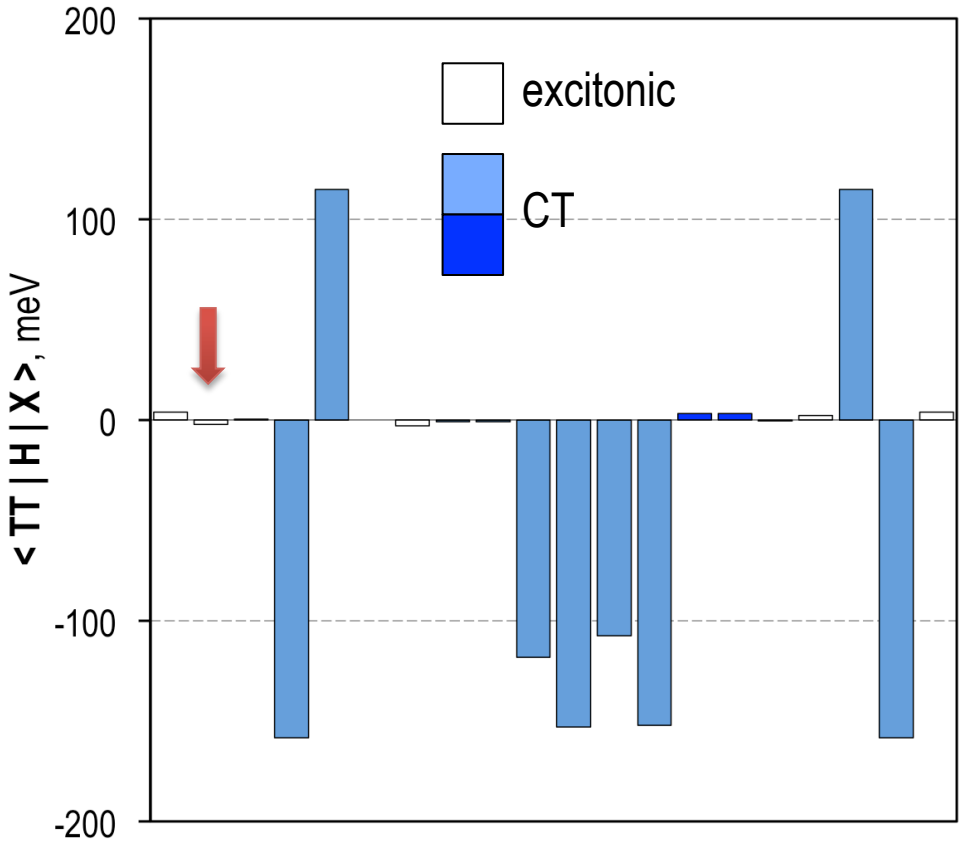




Findings

- Direct coupling very weak
- Largest couplings to CT states

JCTC *10* **2014** 324

Singlet Fission: chromophore coupling

SF transition rate

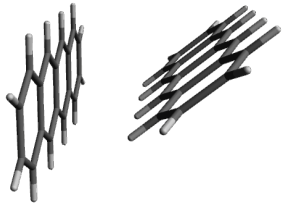
$S_0S_1 \longrightarrow TT$

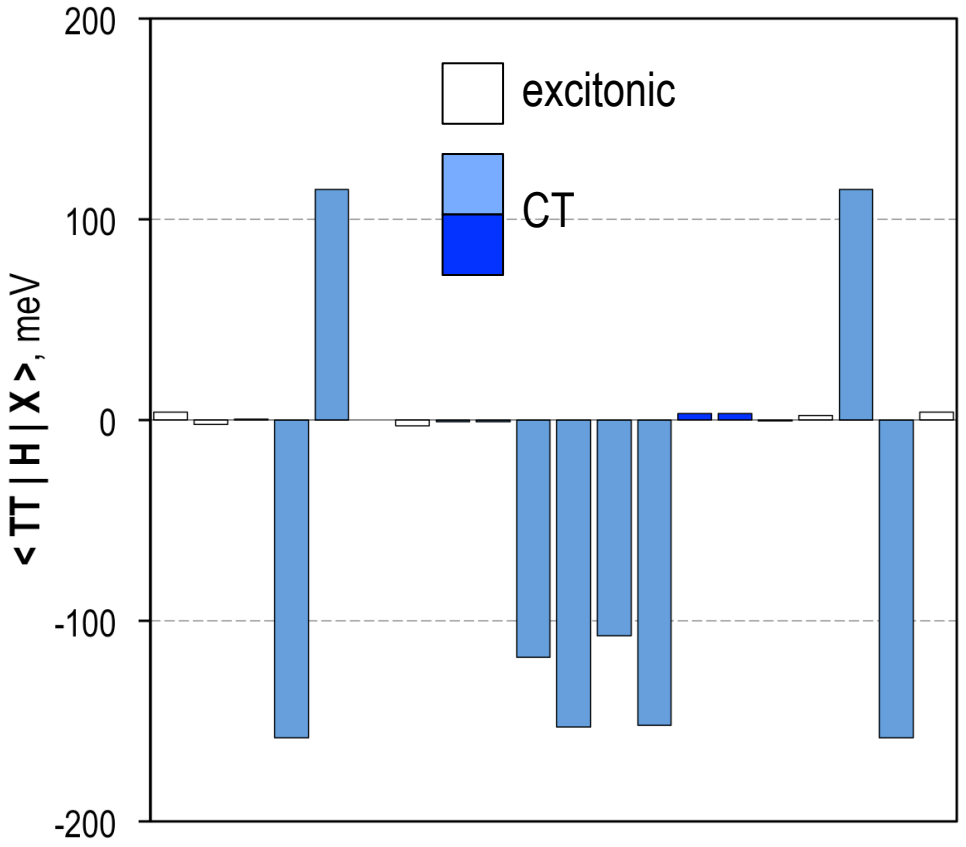
$$\omega(\mathrm{SF}) = \frac{2\pi}{\hbar}\left|\langle TT|\hat{H}|S_0S_1\rangle - \sum_X \frac{\langle TT|\hat{H}|X\rangle\langle X|\hat{H}|S_0S_1\rangle}{\Delta E_X}\right|^2 \rho[E]$$

1st order — direct coupling

2nd order — mediated coupling

Tetracene dimer





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JCTC *10* **2014** 324

Singlet Fission: chromophore coupling

SF transition rate

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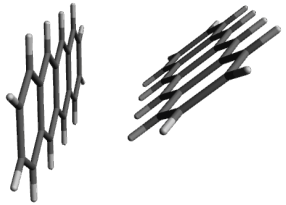
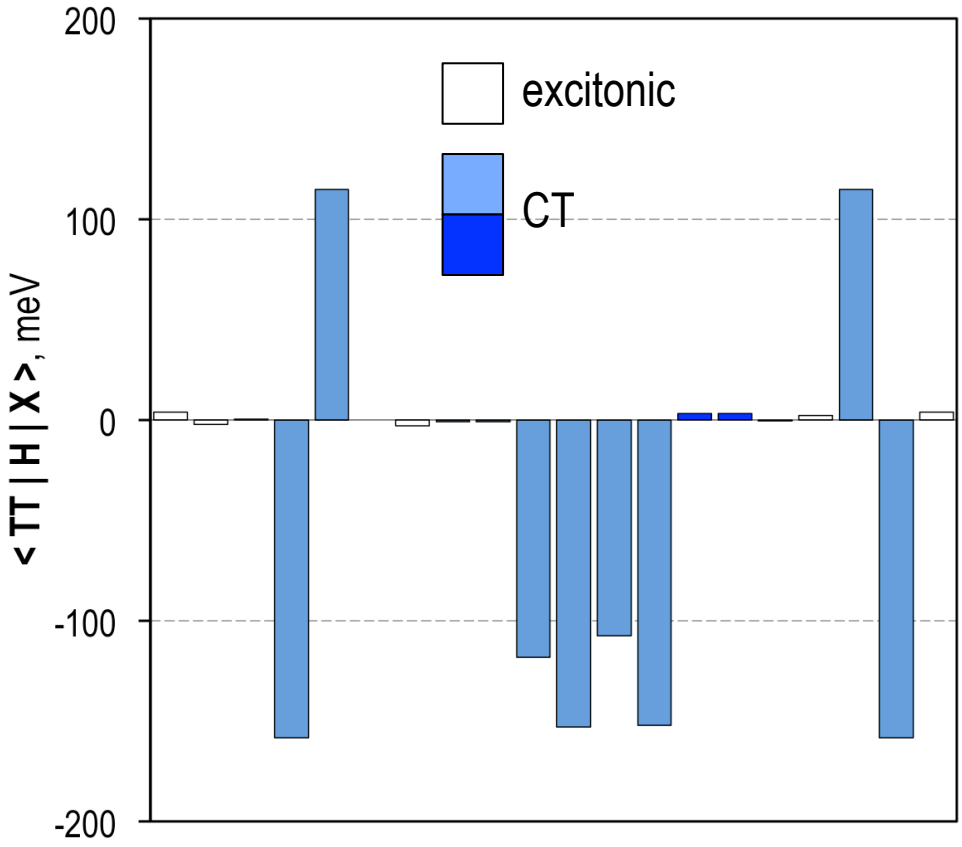
1st order	2nd order
direct coupling	mediated coupling
-2.2 meV	-52.1 meV

Tetracene dimer





Findings

- Direct coupling very weak
- Largest couplings to CT states
- SF mediated by CT states

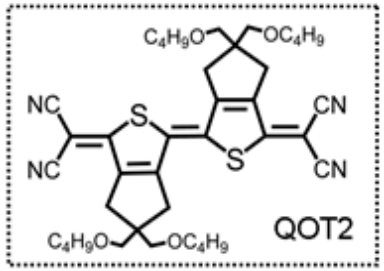
JCTC *10* **2014** 324

Singlet Fission: in one molecule

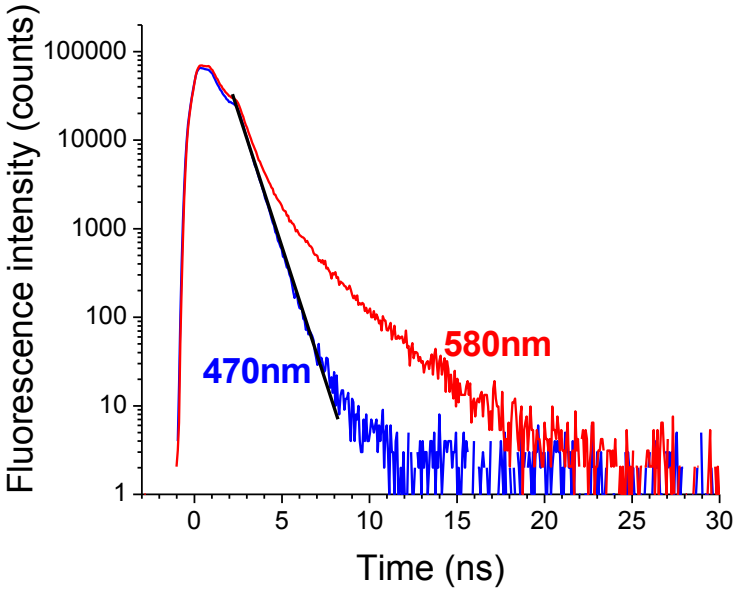
1 molecule
2 chromophores

Singlet Fission: in one molecule

1 molecule
2 chromophores



quinoidal bithiophene



Singlet Fission: in one molecule

1 molecule
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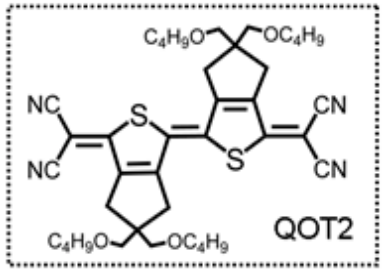
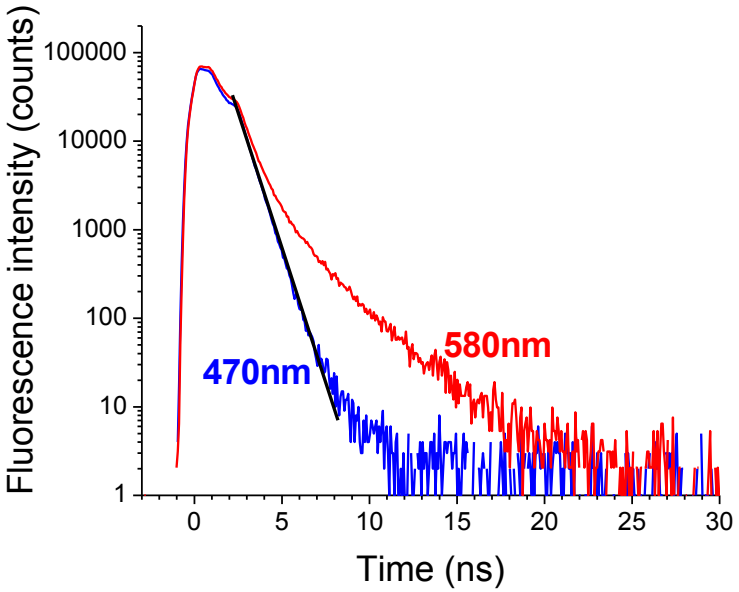


quinoidal bithiophene

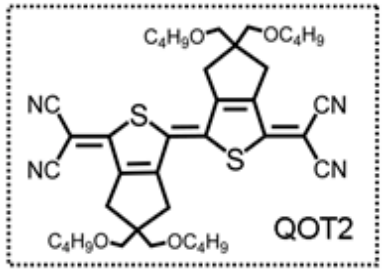
Fission $^1ME \longrightarrow T_1 + T_1$

- Energy gap $\Delta E_F = E[^5ME] - E[^1ME] \rightarrow 0$



Singlet Fission: in one molecule

1 molecule
2 chromophores

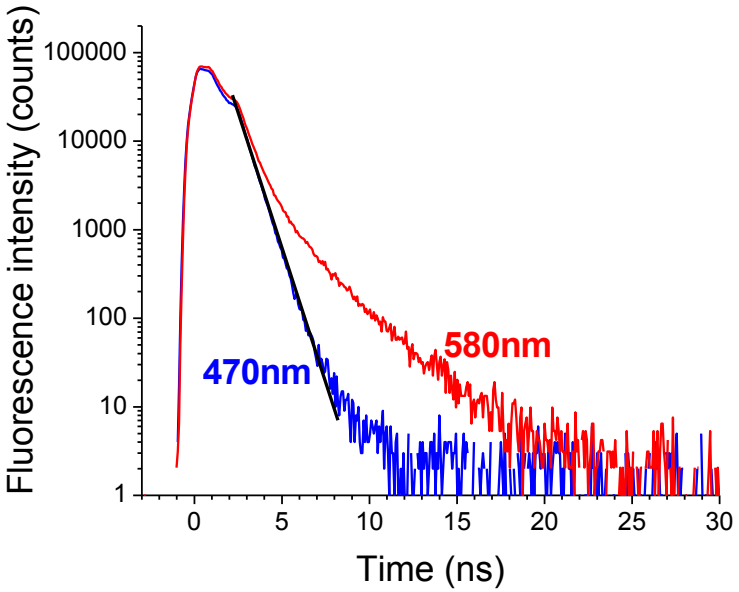


quinoidal bithiophene

Fission $^1ME \longrightarrow T_1 + T_1$

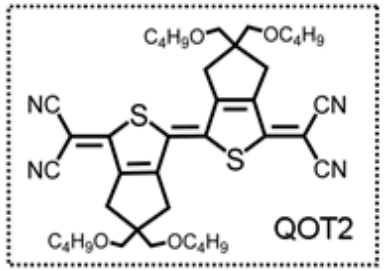
- Energy gap $\Delta E_F = E[^5ME] - E[^1ME] \rightarrow 0$
- % ^1TT $\dfrac{[^1TT]}{[^1ME]} \rightarrow 100\%$

Contribution of ^1TT in the overall ^1ME wavefunction



Singlet Fission: in one molecule

1 molecule
2 chromophores



quinoidal bithiophene

Fission $^1ME \longrightarrow T_1 + T_1$

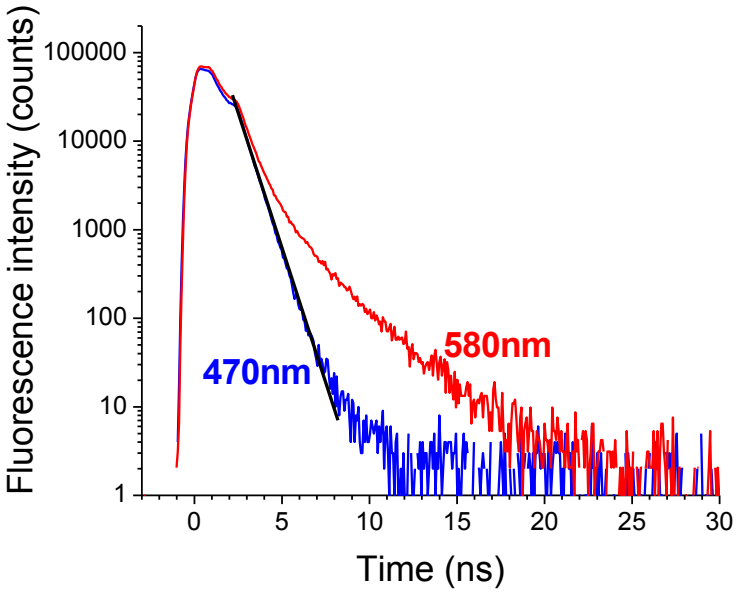
- Energy gap $\Delta E_F = E[^5ME] - E[^1ME] \rightarrow 0$

- % ^1TT $\frac{[^1TT]}{[^1ME]} \rightarrow 100\%$

  Contribution of ^1TT in the overall ^1ME wavefunction

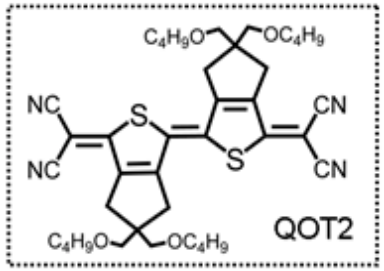
- Radical character $N_U = \sum_i 1 - |1 - n_i| \qquad N_U \rightarrow 4$

  Number of unpaired electrons of ^1ME



Singlet Fission: in one molecule

1 molecule
2 chromophores



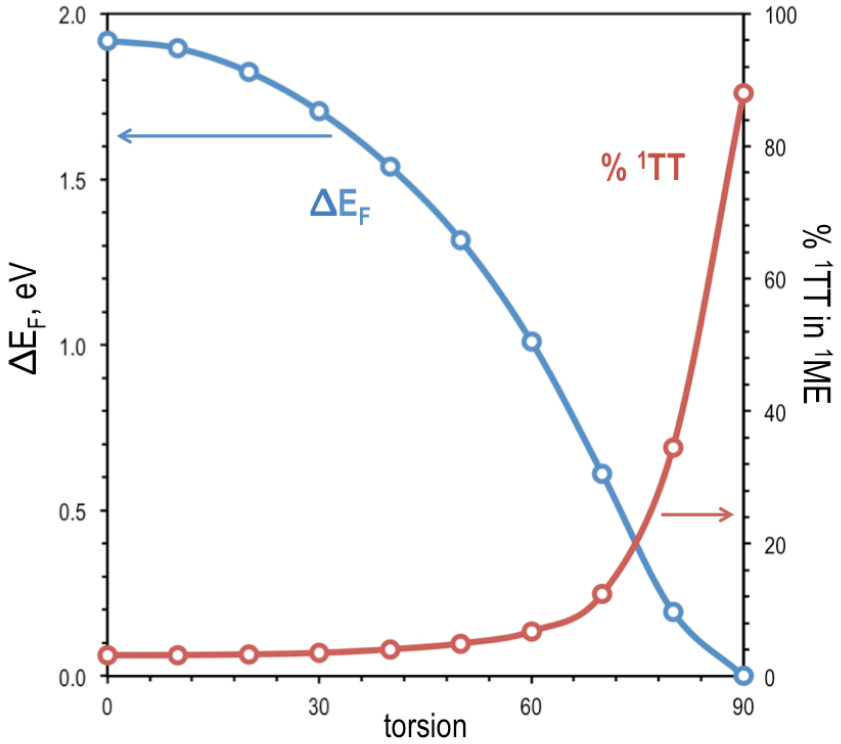
quinoidal bithiophene

Fission ^{1}ME $\longrightarrow$ $T_1 + T_1$

- Energy gap $\Delta E_F = E[^5ME] - E[^1ME] \rightarrow 0$
- % ^{1}TT $\dfrac{[^1TT]}{[^1ME]} \rightarrow 100\%$

  Contribution of ^{1}TT in the overall ^{1}ME wavefunction
- Radical character $N_U = \sum_i 1 - |1 - n_i| \quad N_U \rightarrow 4$

  Number of unpaired electrons of ^{1}ME



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Collaborations

- Theodore Goodson (U. Michigan)
- Juan Casado (U. Malaga)

] QOT2

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Research Fellowship

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