

Covalently Linked Tetracene Dimers for Singlet Fission

Jamie Snyder

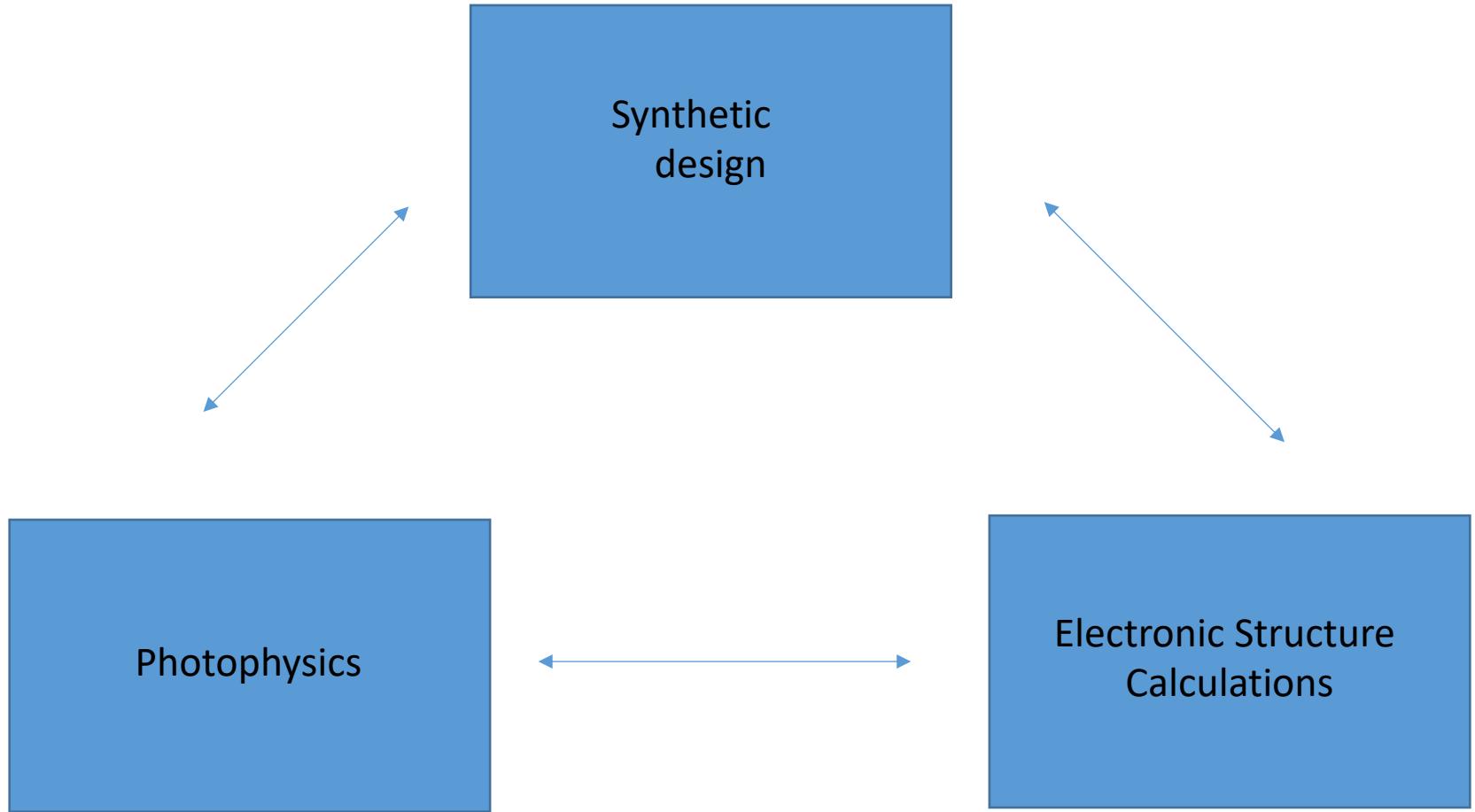
University of Colorado Boulder

2015 July 02

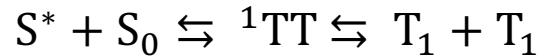
A photograph of a winter landscape. In the foreground, there's a large tree trunk on the left and a snow-covered ground. In the middle ground, there are several houses and trees covered in snow. In the background, there are majestic mountains under a clear blue sky.

~300 Day of sun*

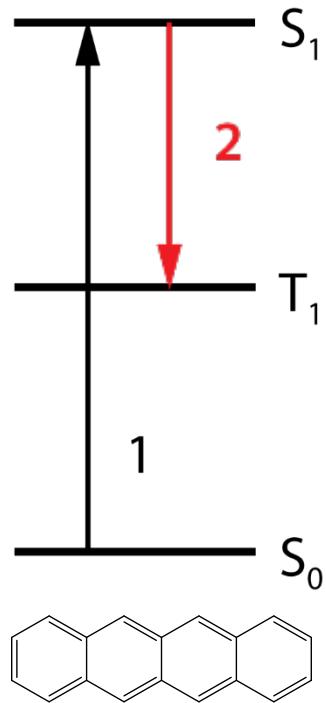
*at least one hour



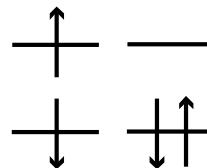
Singlet Fission



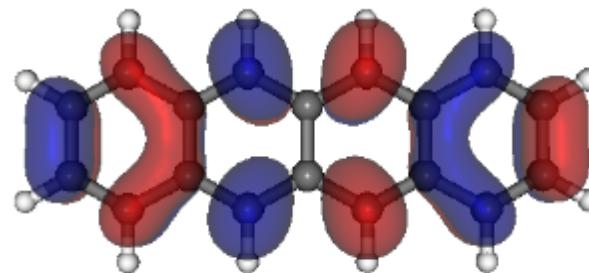
State Picture



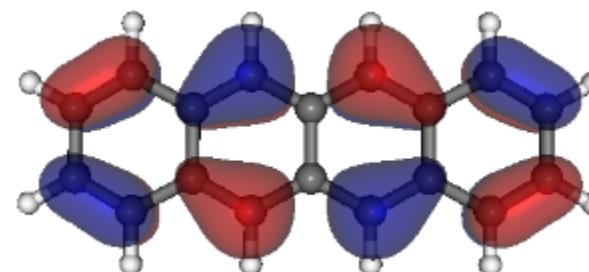
Orbital



HOMO \rightarrow LUMO

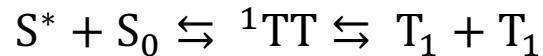


LUMO



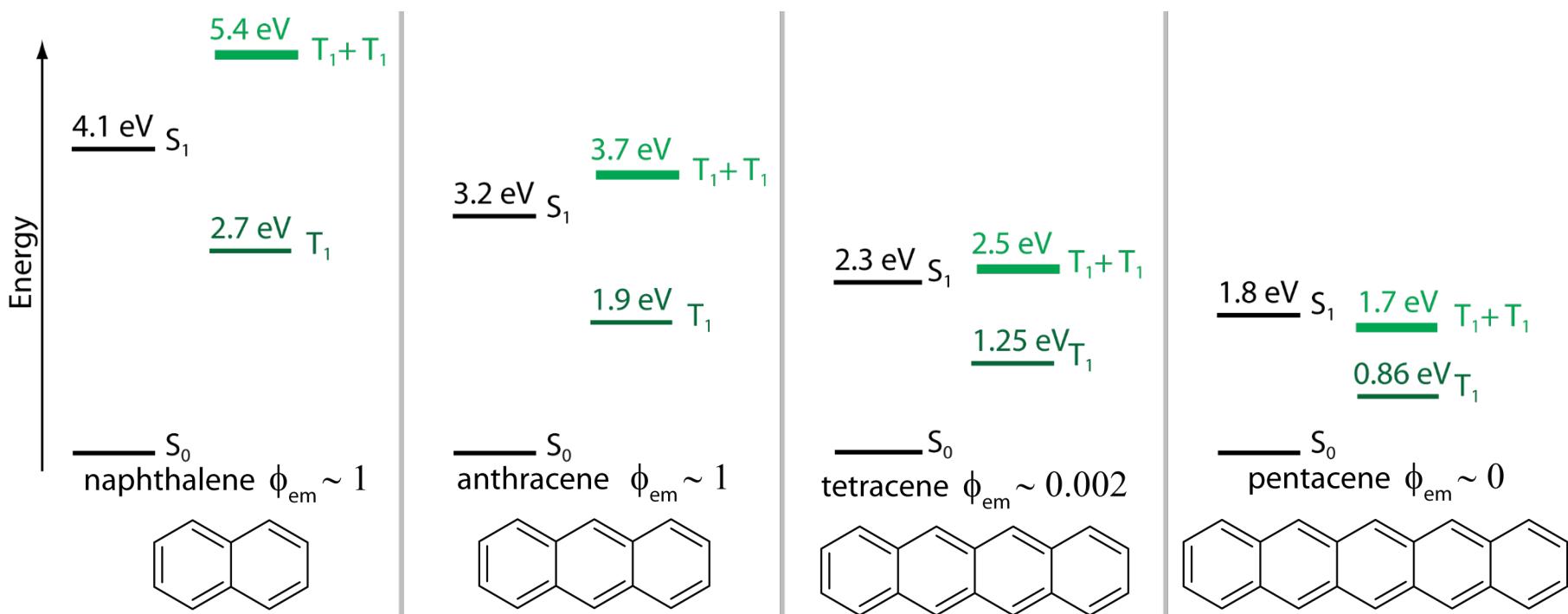
HOMO

Singlet fission – Molecular Systems

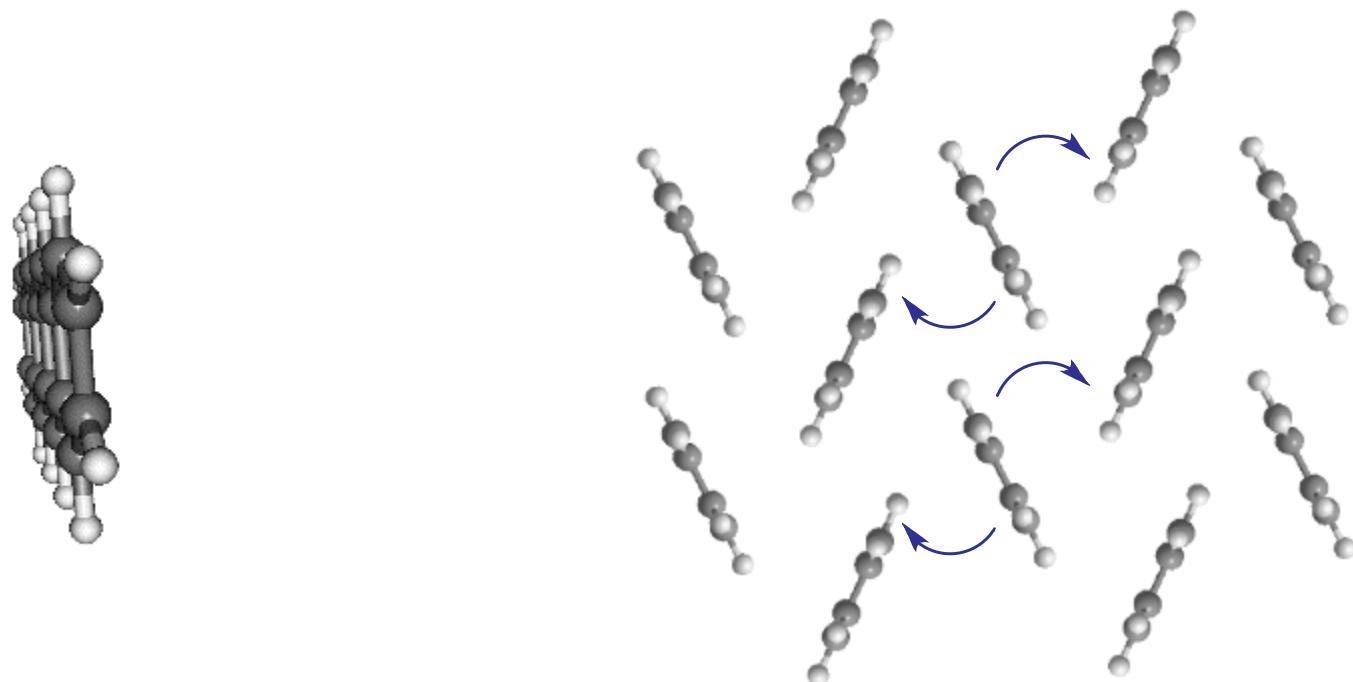


$$\Delta E_{SF} = E({}^1\text{TT}) - E(S_1)$$

$$\Delta E_{SF} = 2xE(T_1) - E(S_1)$$

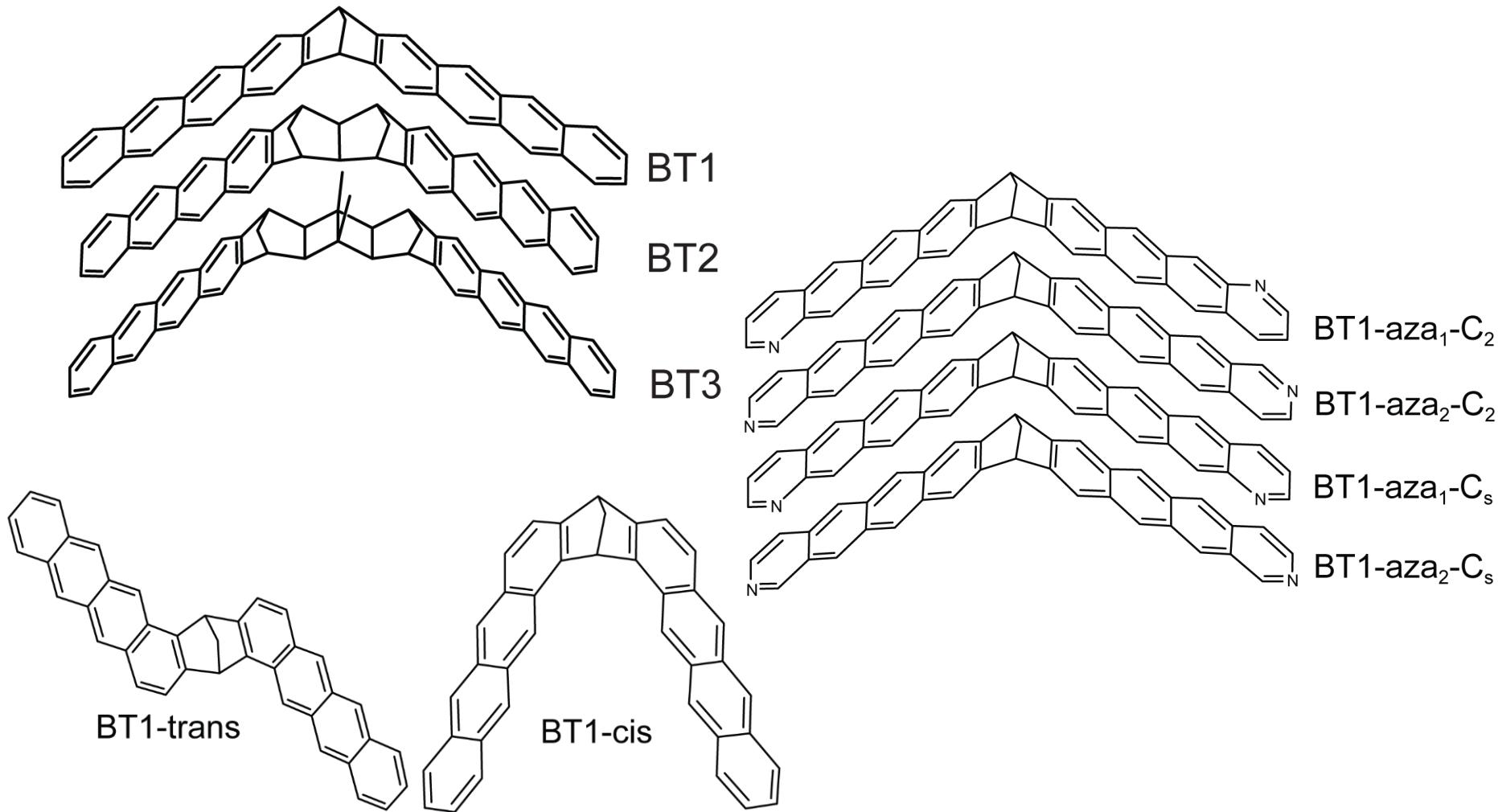


Singlet Fission in Polyacene Crystals

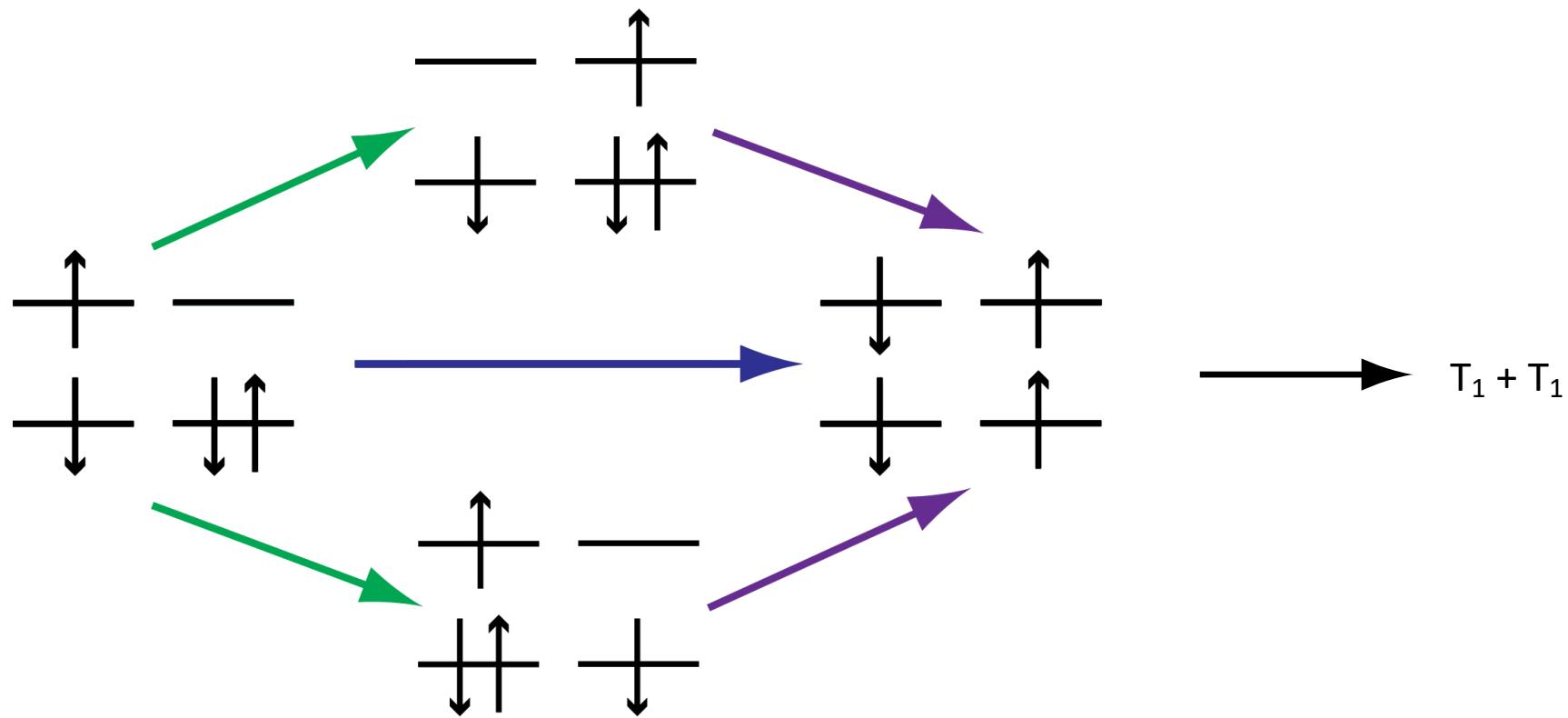


can we use this information to build molecular dimers?

Singlet Fission in Dimeric Systems

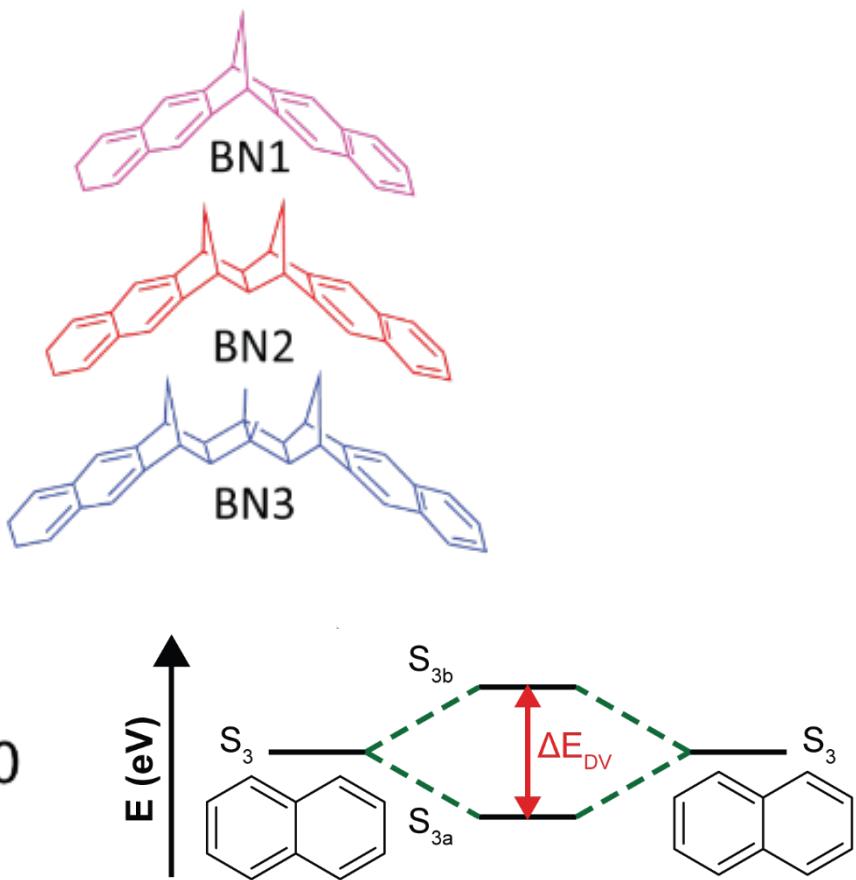
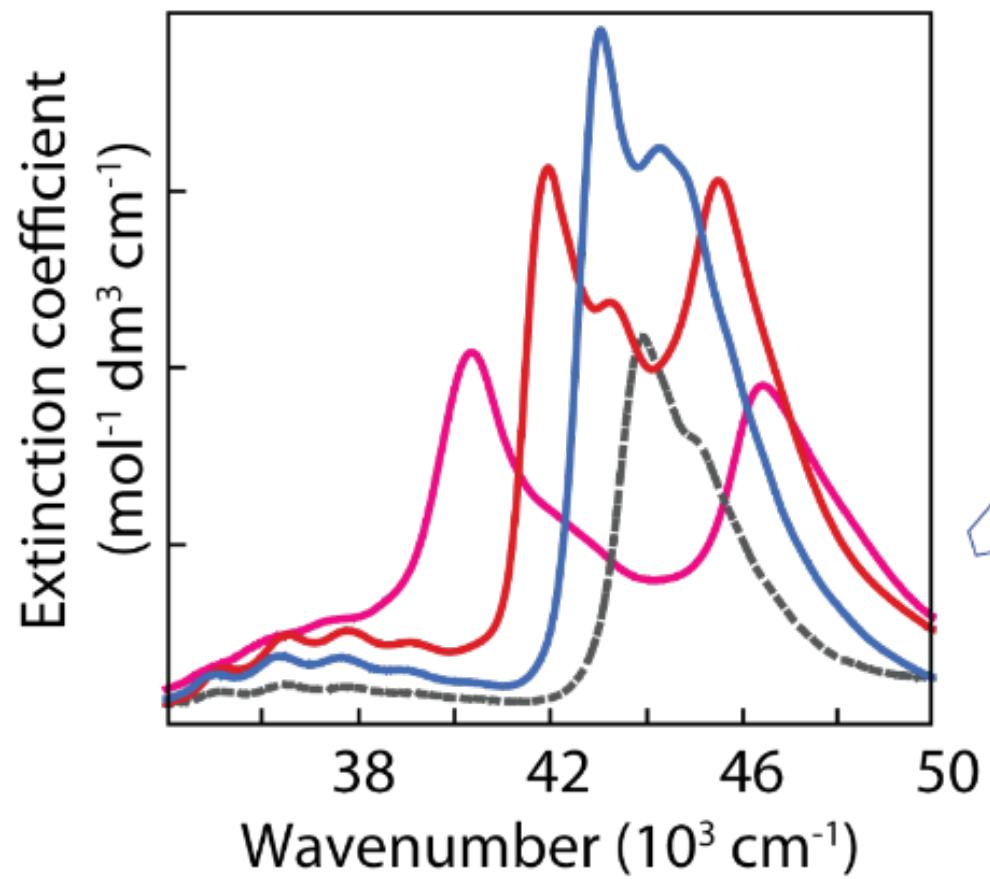


Proposed Mechanism

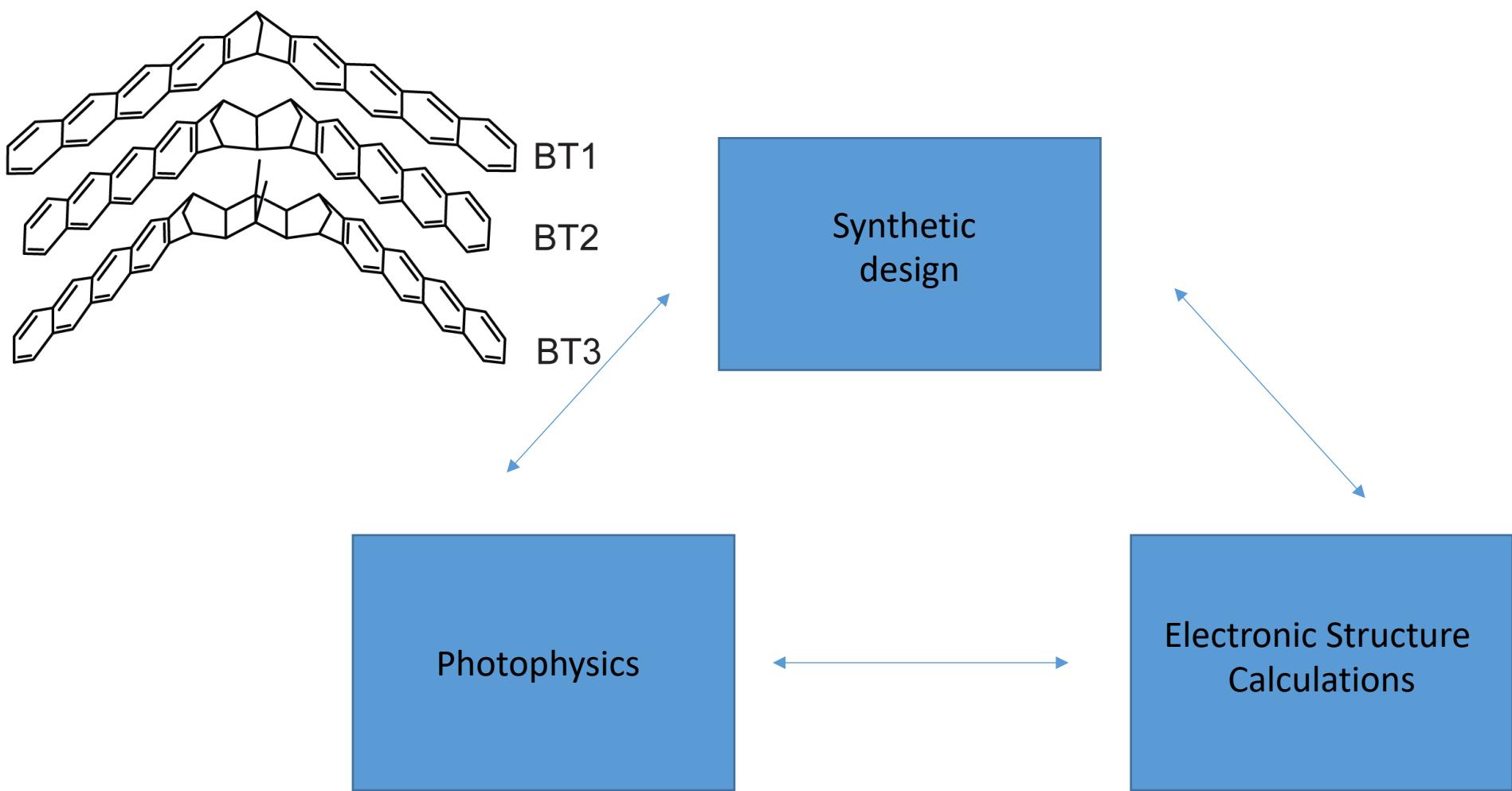


What kind of interactions are important to SF?

Electronic Interactions – Davydov Splitting



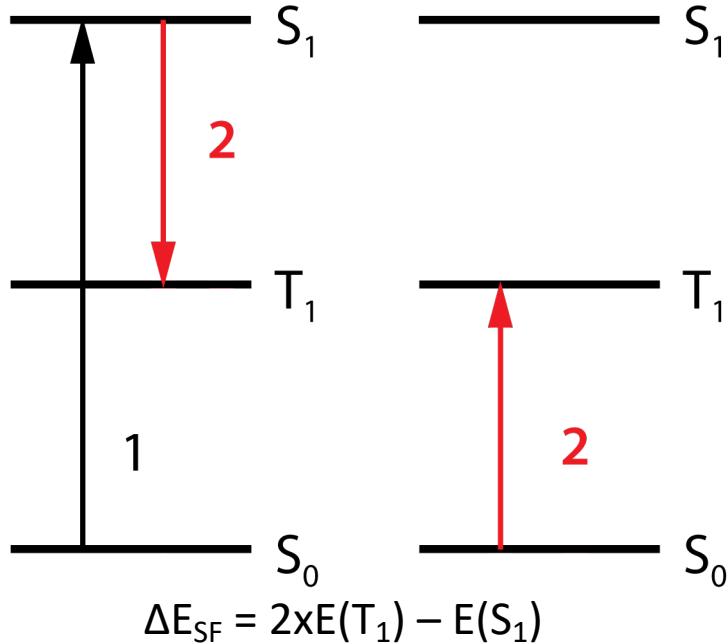
Molecular Design – BT1-BT3



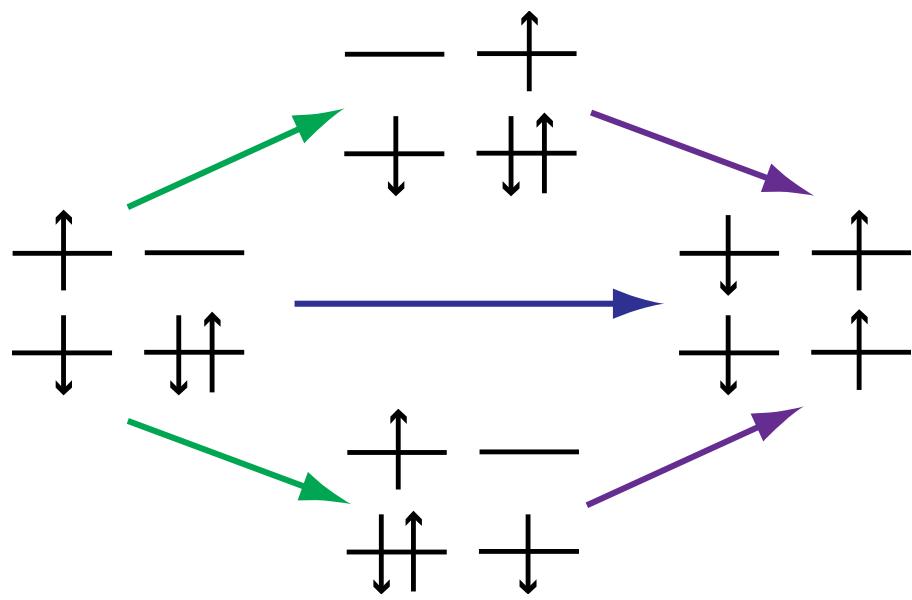
Electronic Structure – Driving Force

what states do we need?

State picture



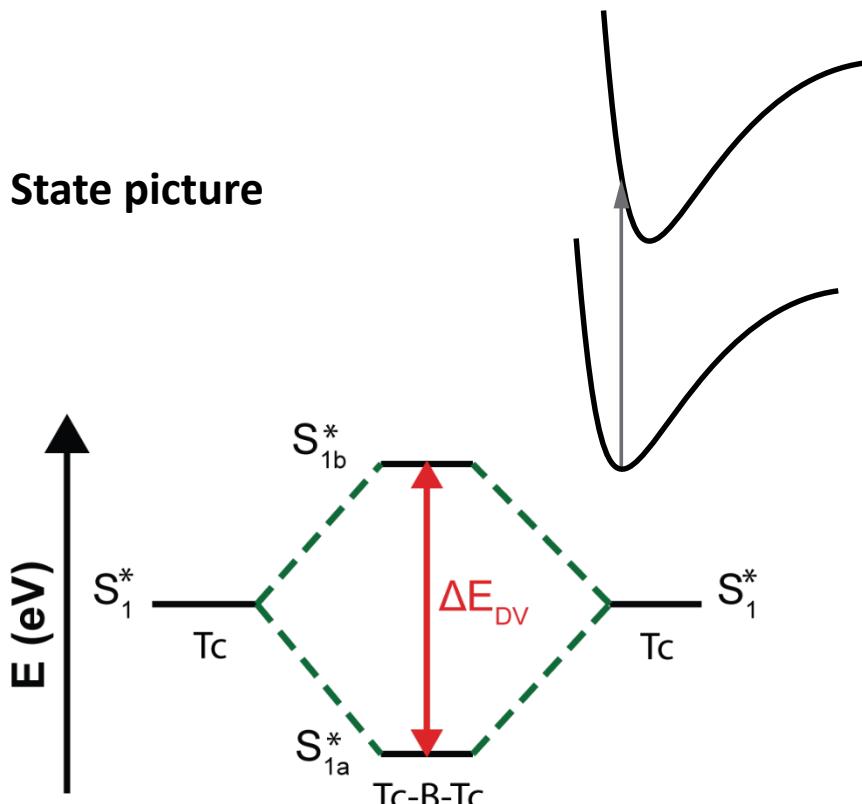
Orbital picture



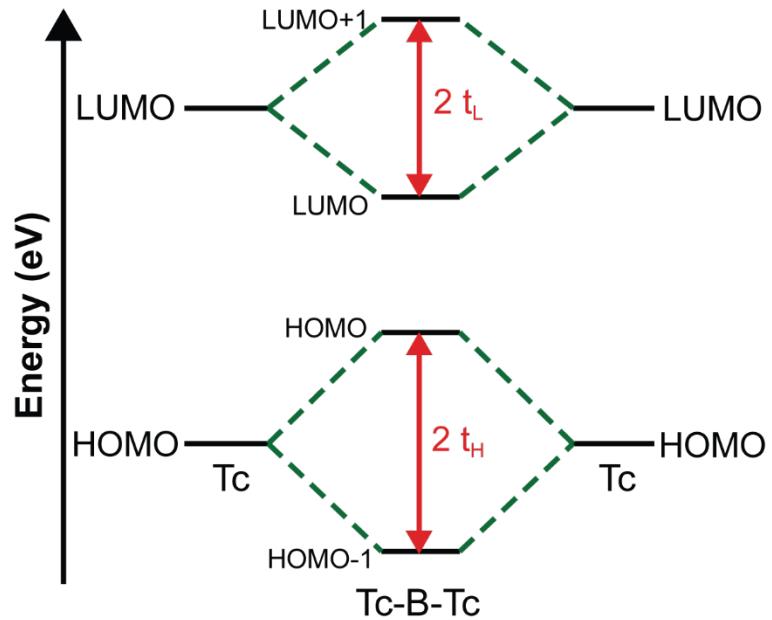
states – S_0 , S_1 , T_1 , CT

Electronic Structure – Electronic Interactions

State picture

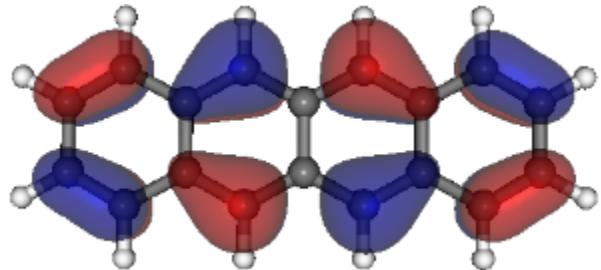


Orbital Picture

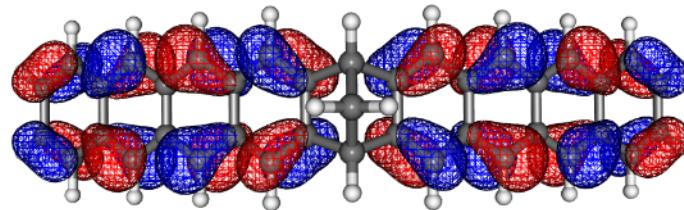
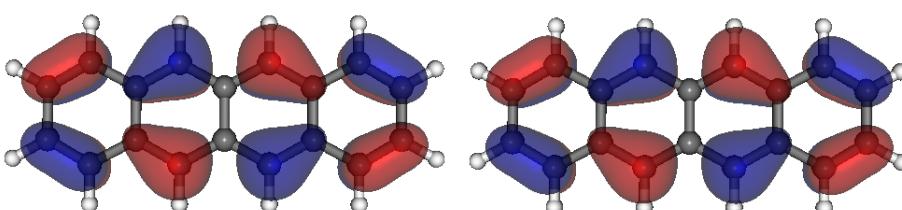
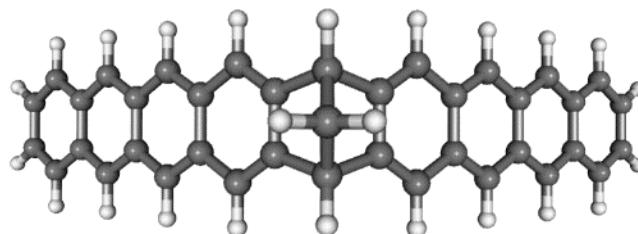
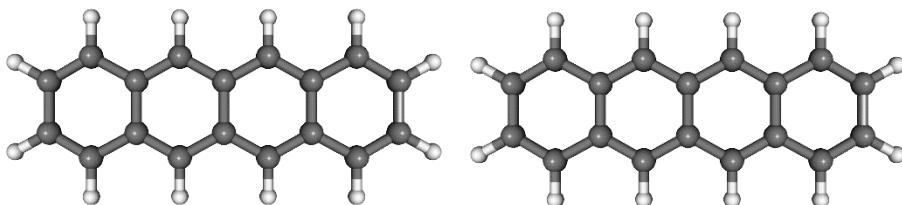
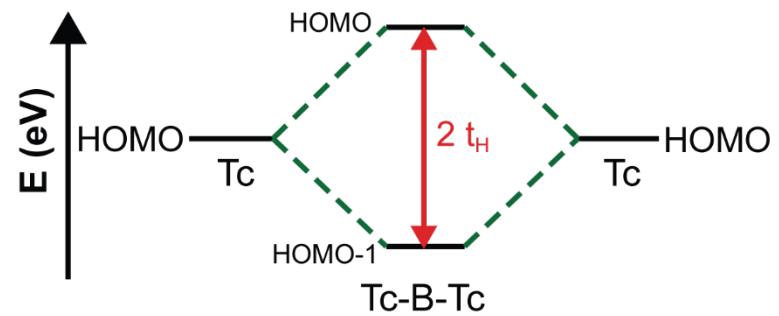


e^- coupling – ΔE_{DV} , t_H , t_L

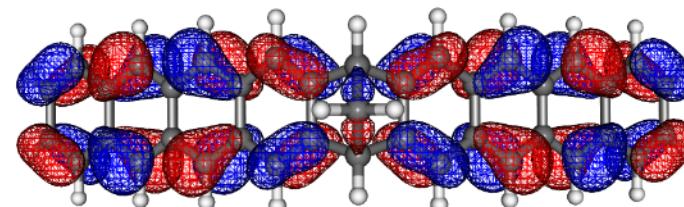
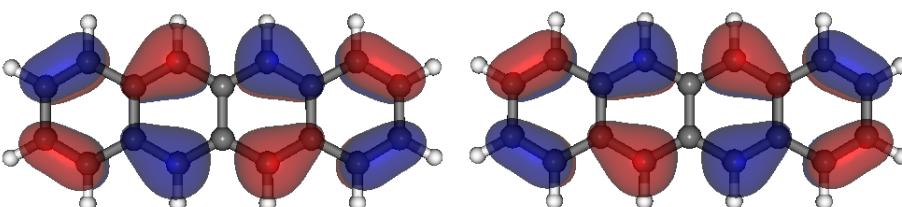
Building the frontier Orbitals



HOMO

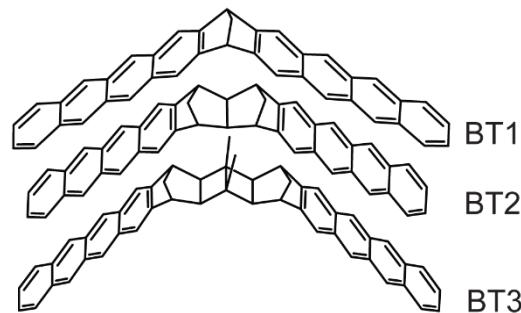


HOMO

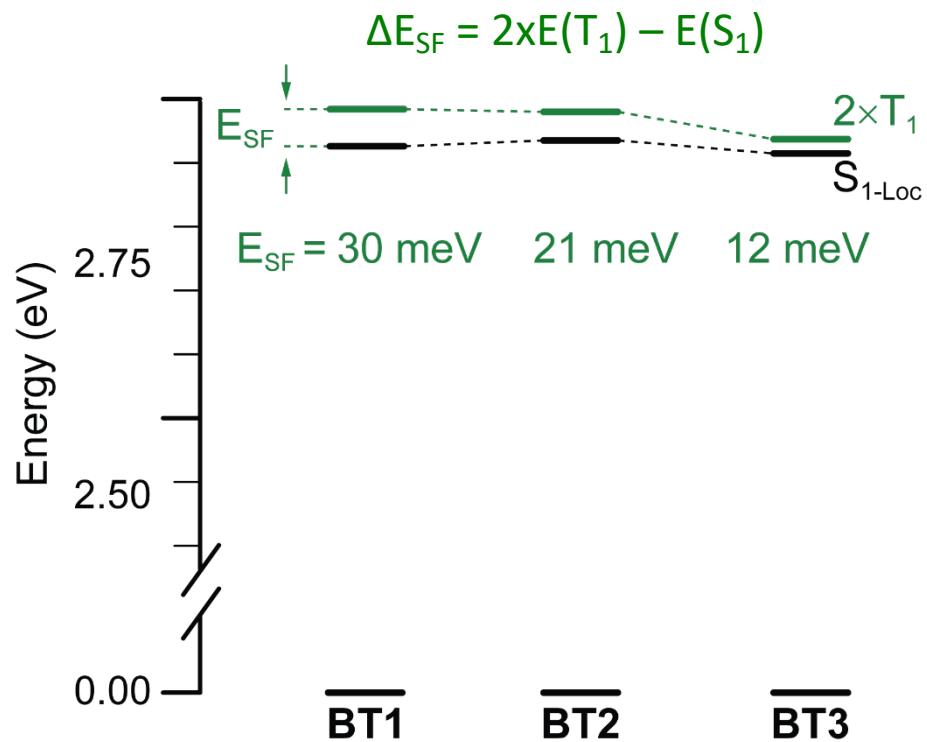


HOMO-1

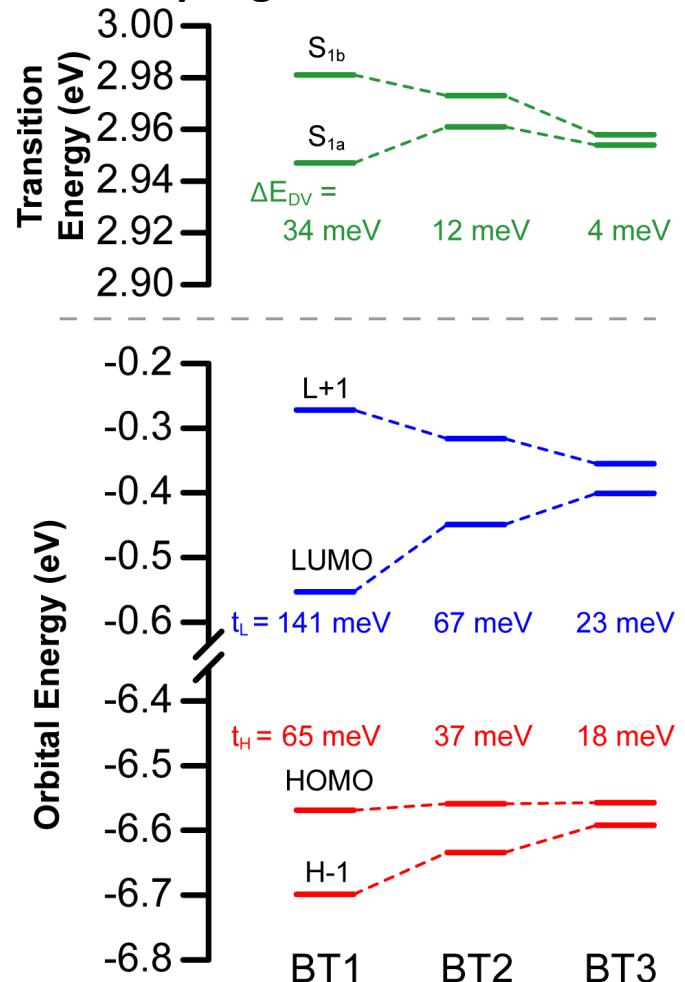
Electronic Structure – BT1-BT3 series



Driving Force

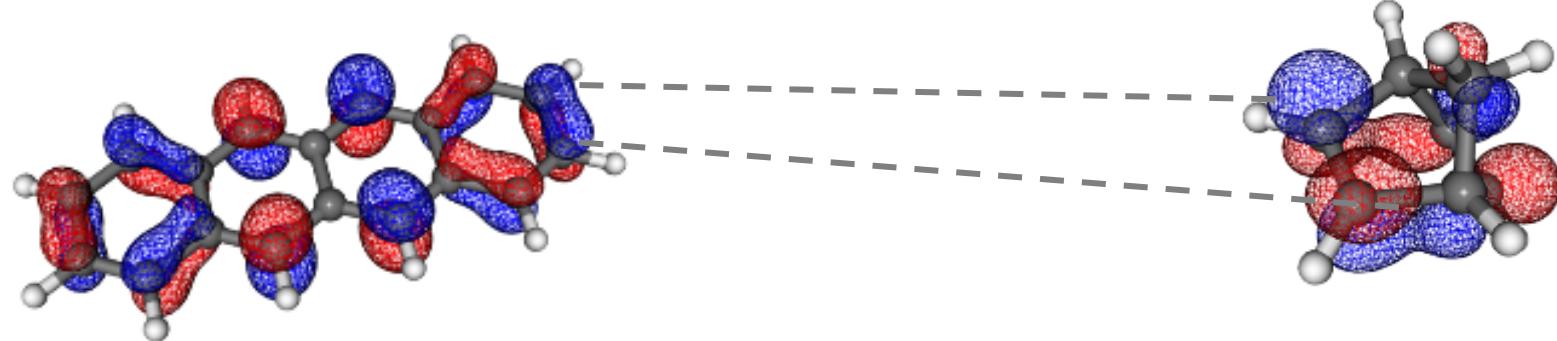


Electronic Coupling

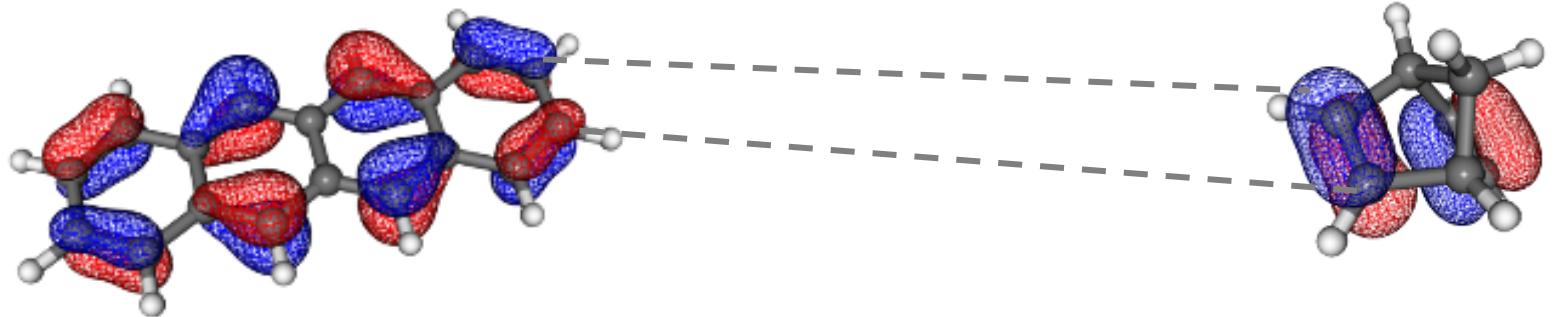


Symmetry and orbitals on the norbornyl-bridge

LUMO

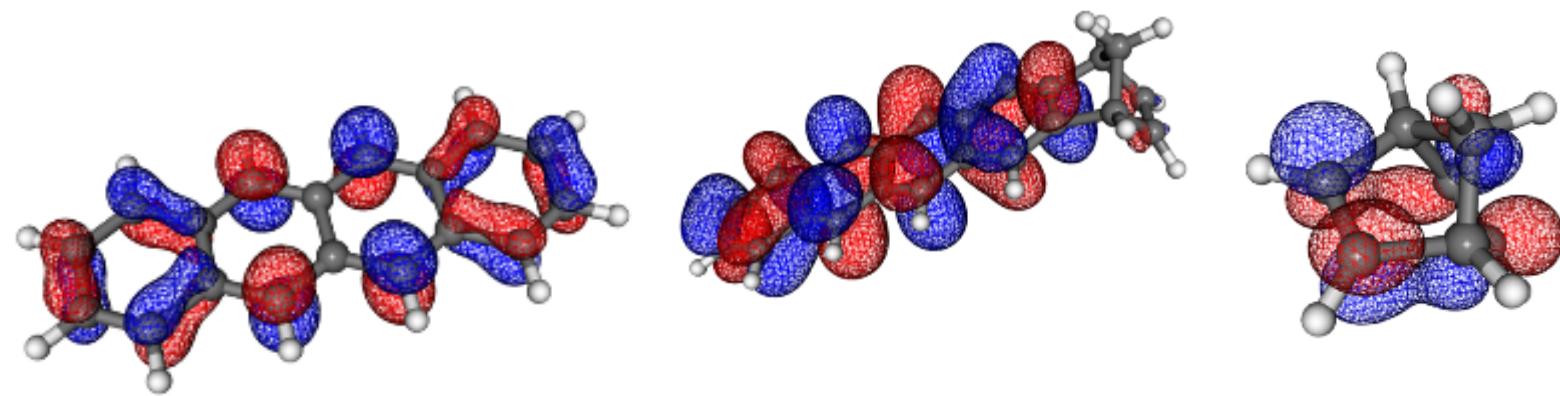


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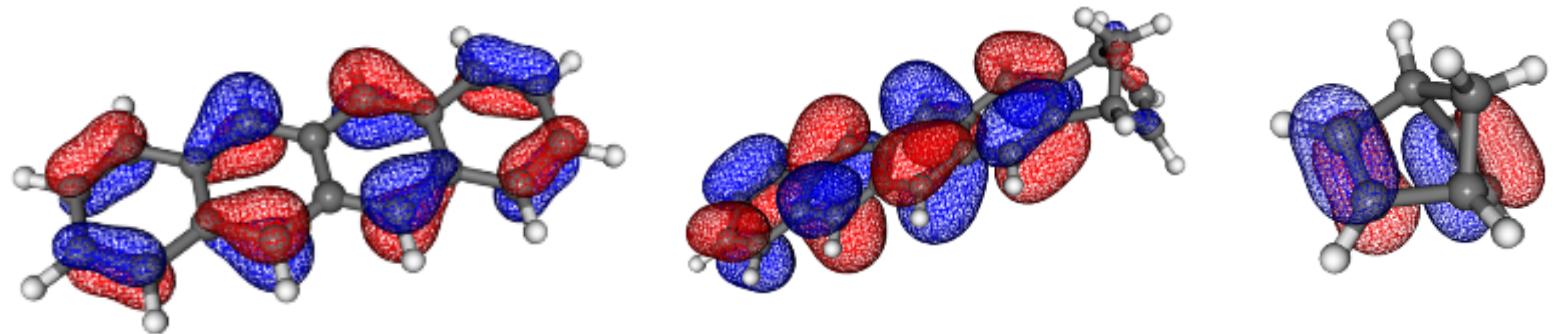


Symmetry and orbitals on the norbornyl-bridge

LUMO

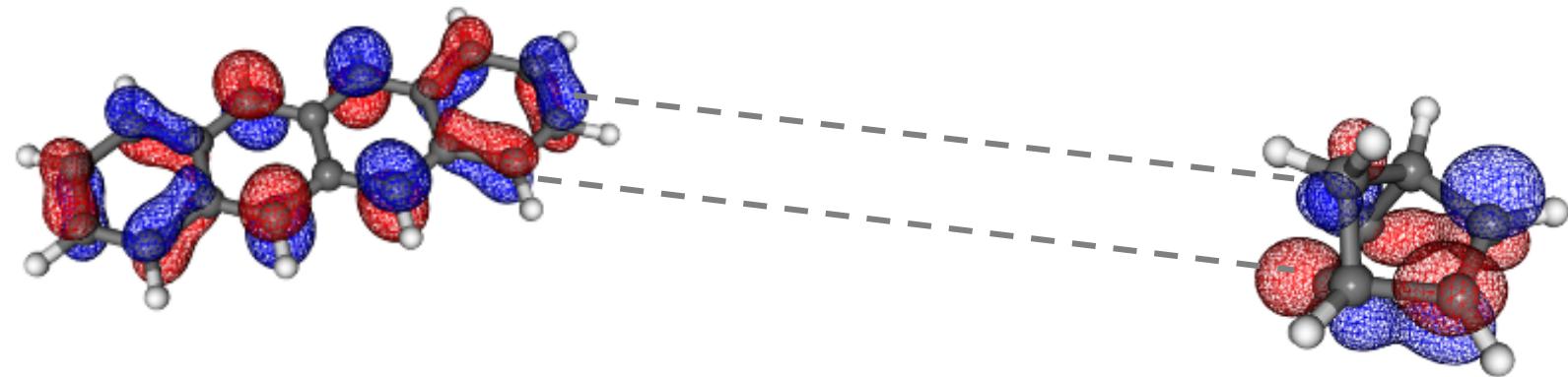


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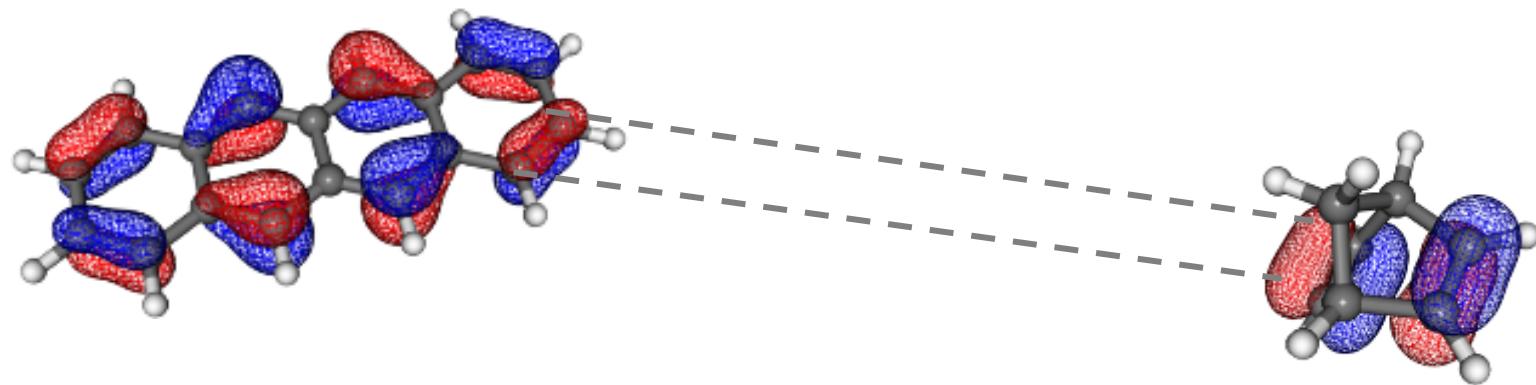


Symmetry and orbitals on the norbornyl-bridge

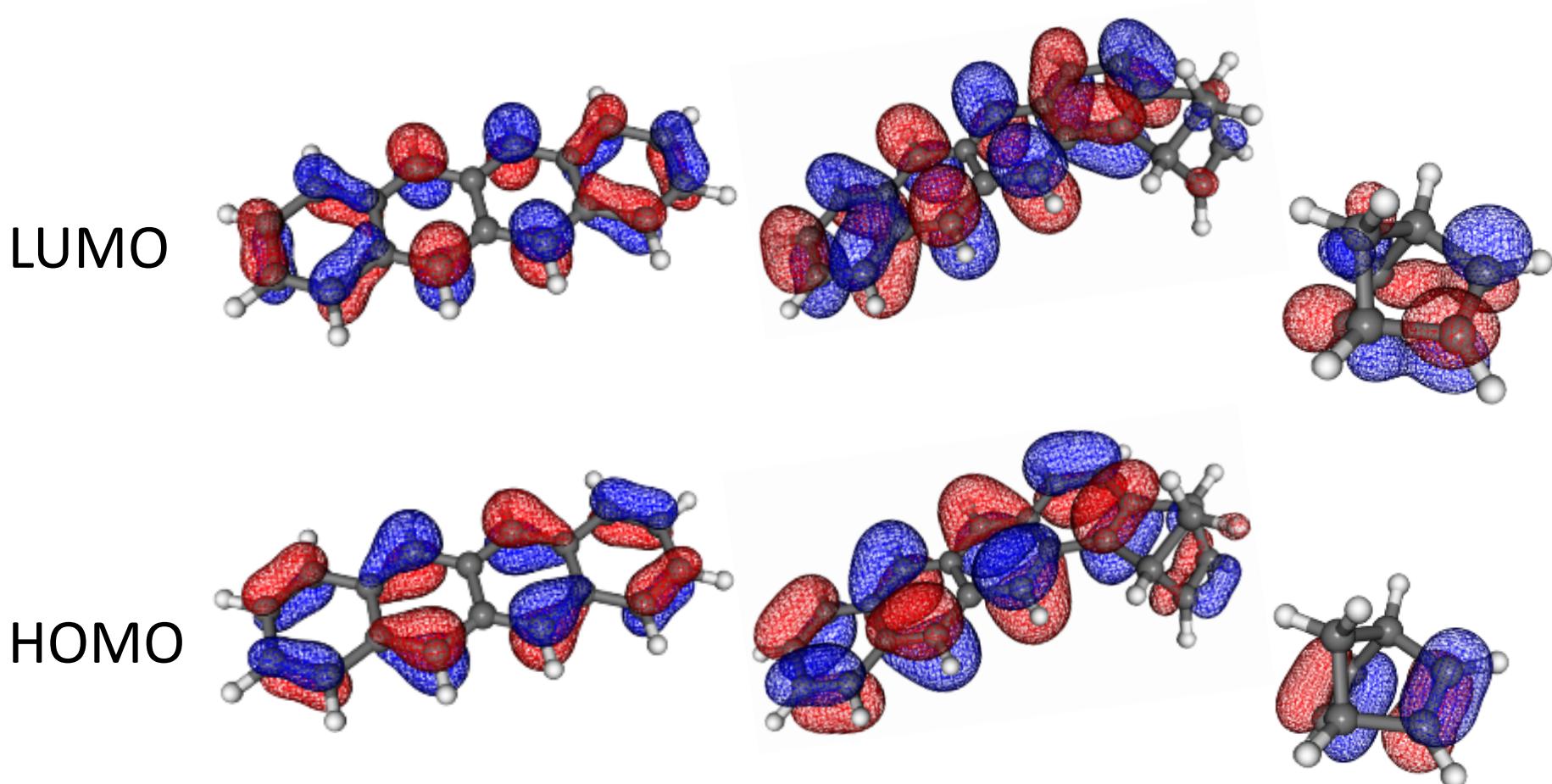
LUMO



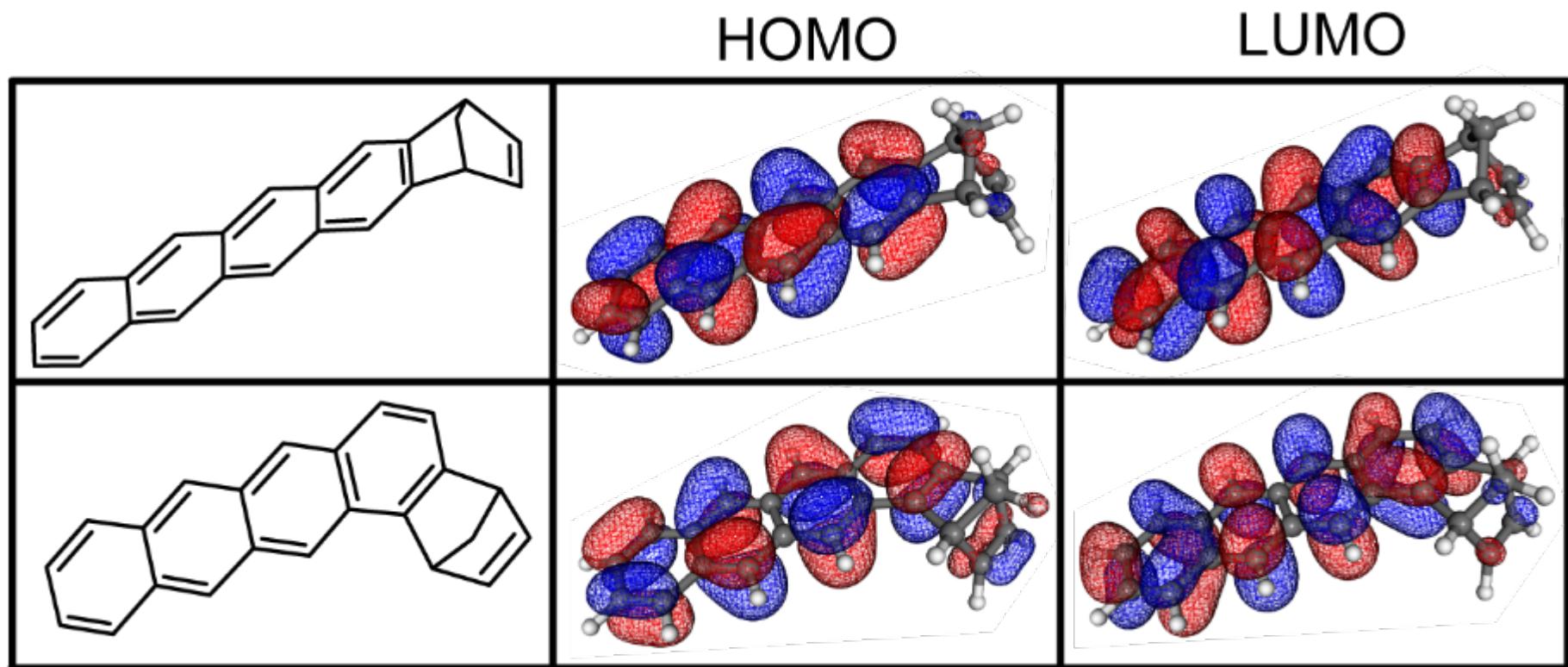
HOMO



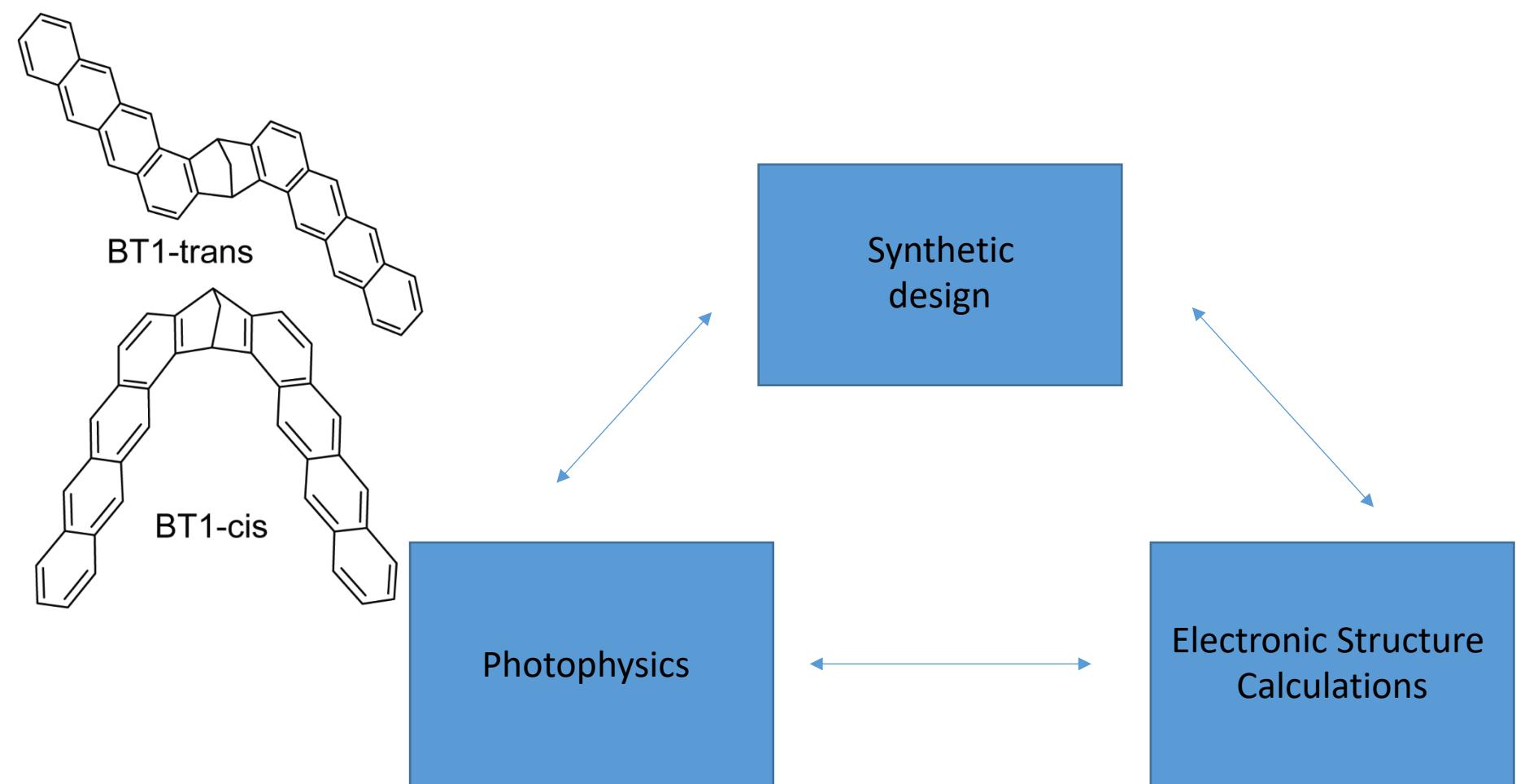
Symmetry and orbitals on the norbornyl-bridge



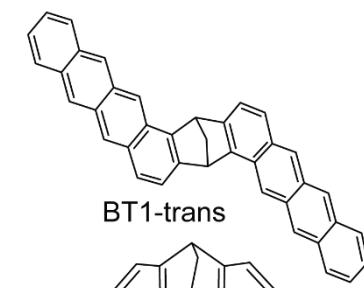
Symmetry and orbitals on the norbornyl-bridge



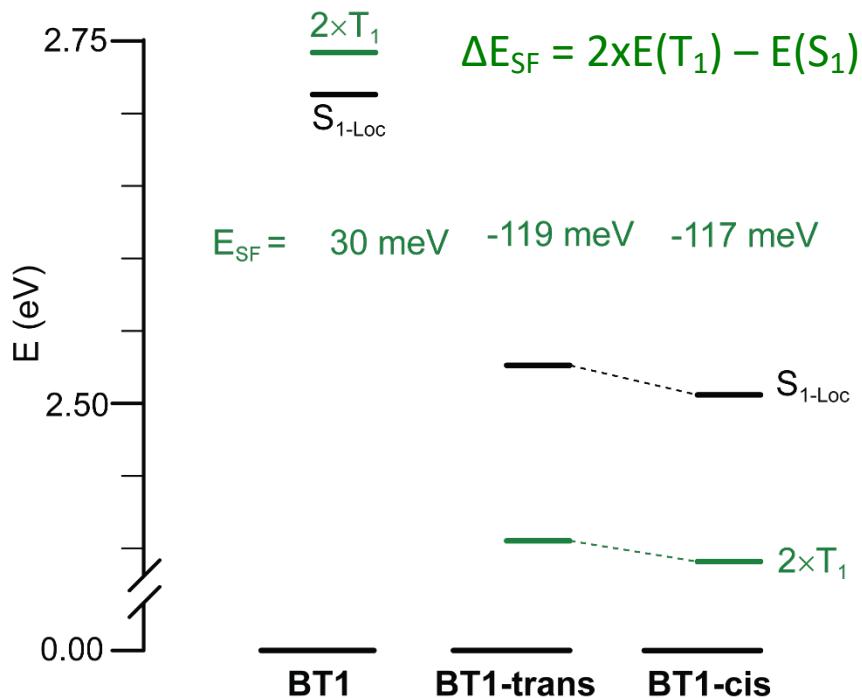
Molecular Design – BT1-cis and BT1-trans



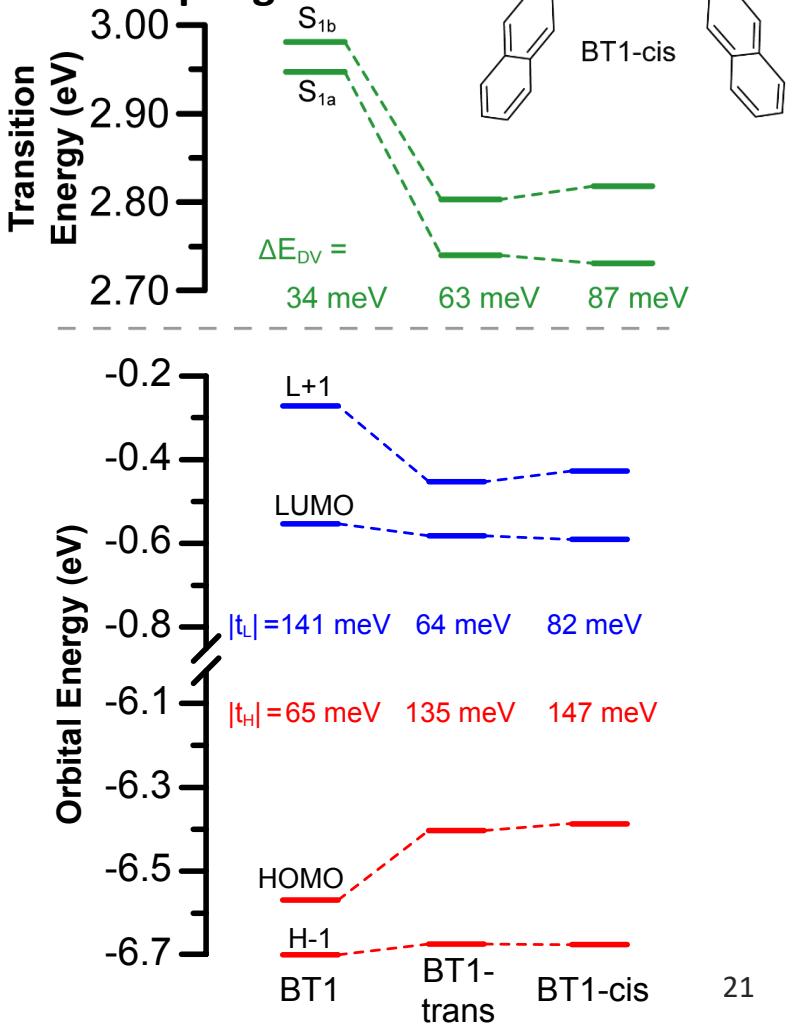
Electronic Structure – BT1-trans & BT1-cis



Driving Force

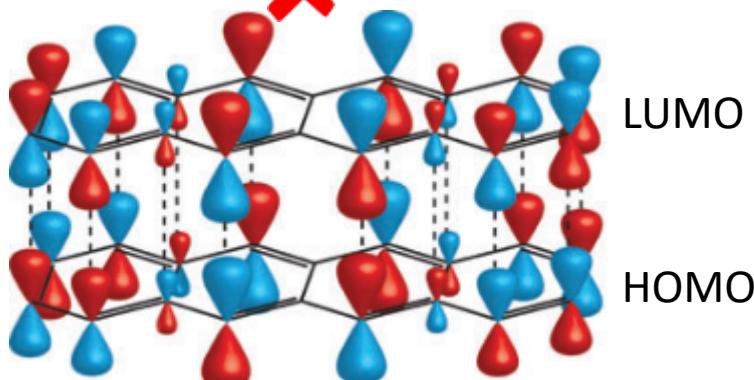


Electronic Coupling

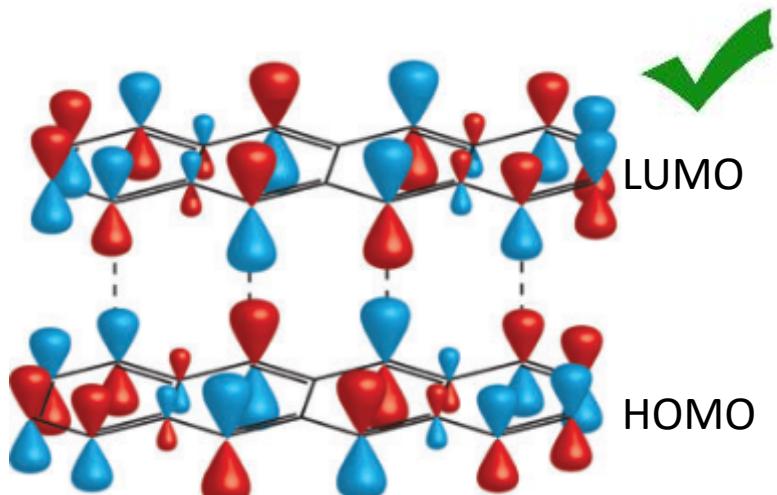


Symmetry constraints

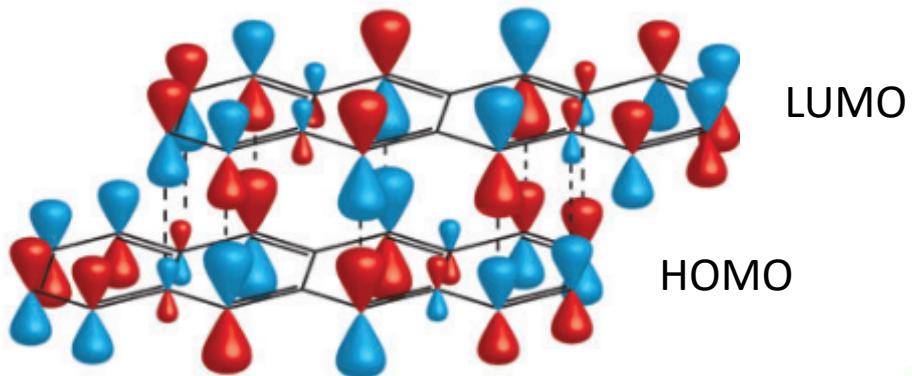
stacked



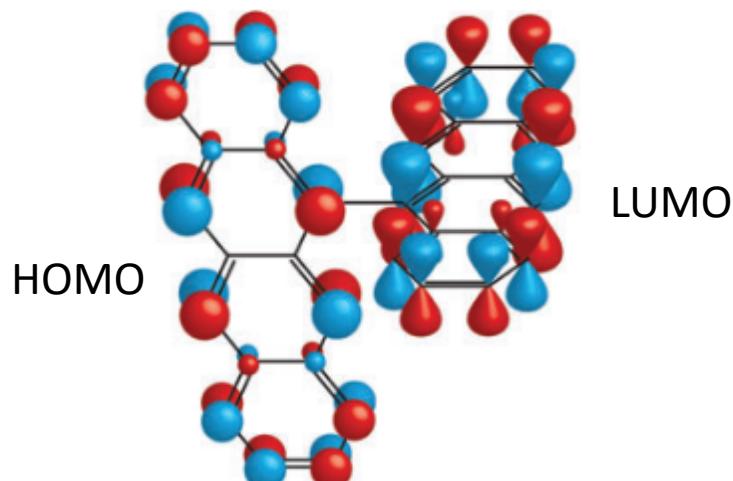
slip-stacked $\perp h \rightarrow l$ transition



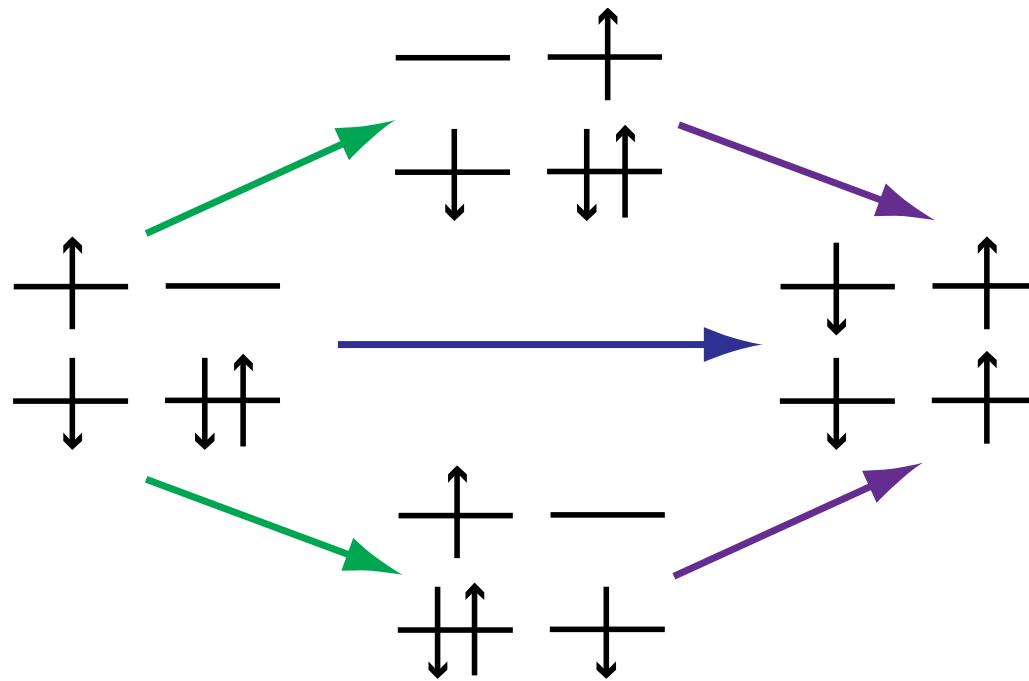
slip-stacked $\parallel h \rightarrow l$ transition



covalently linked



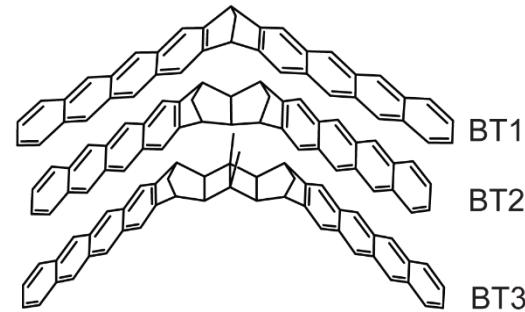
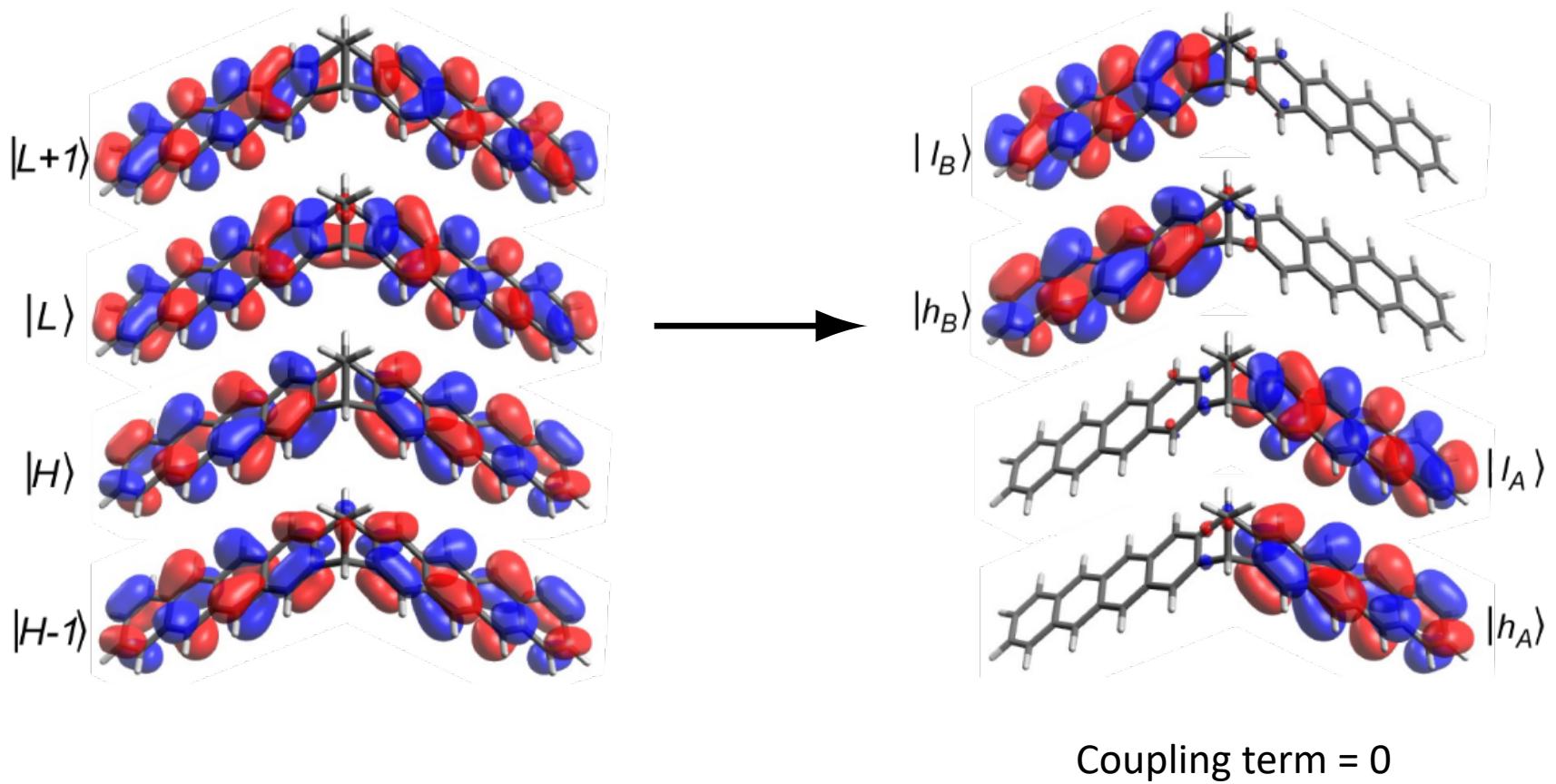
Communication between the states



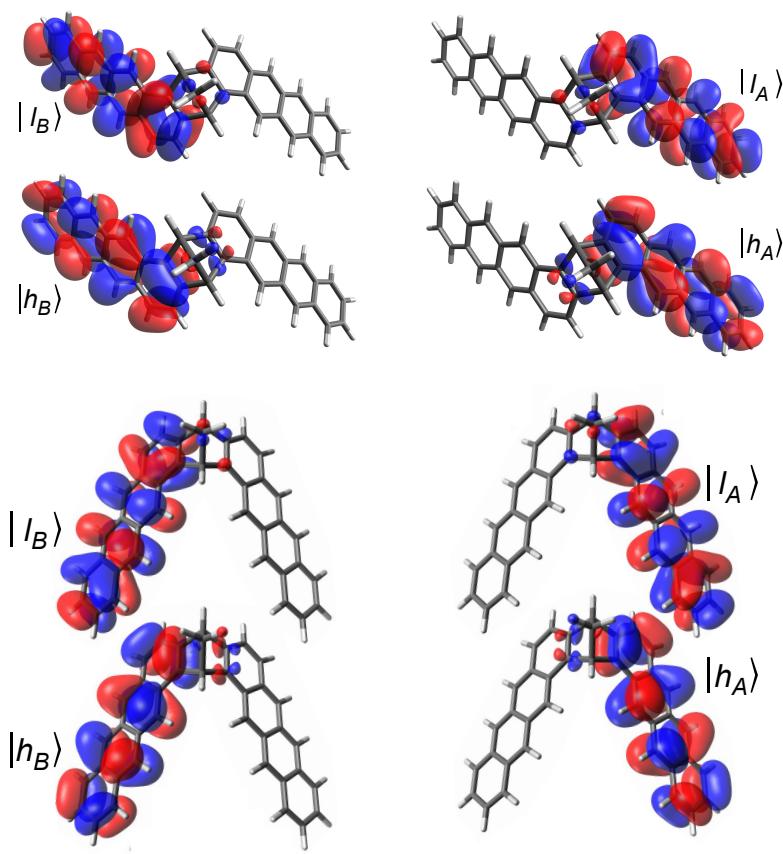
$$rate \approx \left(\frac{3\pi}{\hbar} \right) \left| \frac{\langle l_A | F | h_B \rangle \langle l_A | F | l_B \rangle - \langle h_A | F | l_B \rangle \langle h_A | F | h_B \rangle}{\Delta E_{CT}^2} \right|^2 \rho[E]$$

$$\text{Coupling term} = \frac{\left| \sqrt{3/2} (t_{HL} t_{LL} - t_{LH} t_{HH}) \right|}{\Delta E_{CT}}$$

One-electron Coupling— Boys and Redigonalization

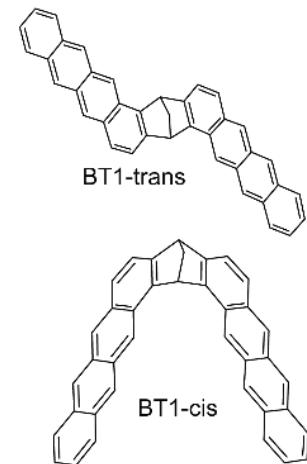


One-electron Coupling



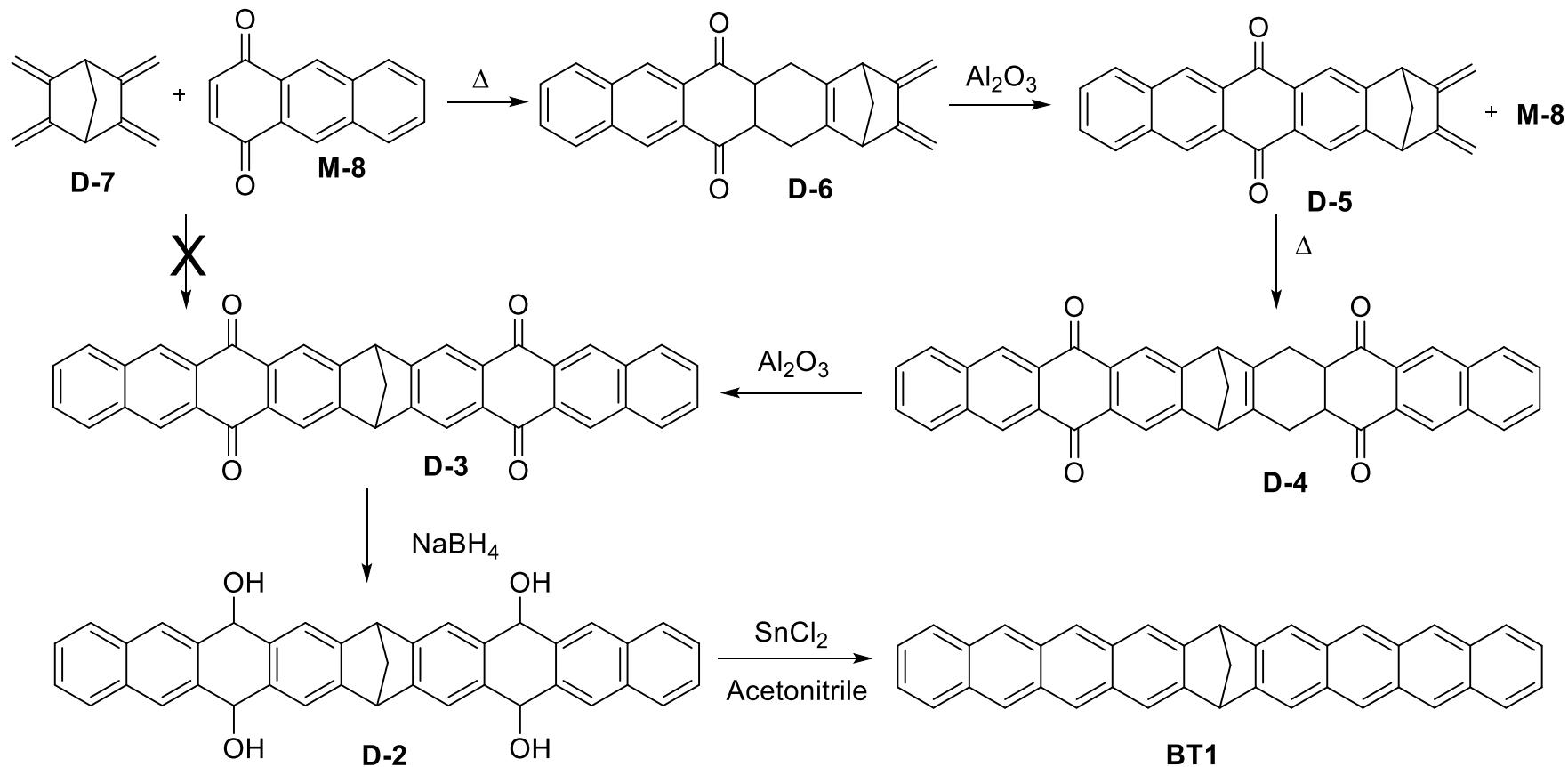
Coupling term = 2.2 meV

Coupling term = 0.4 meV

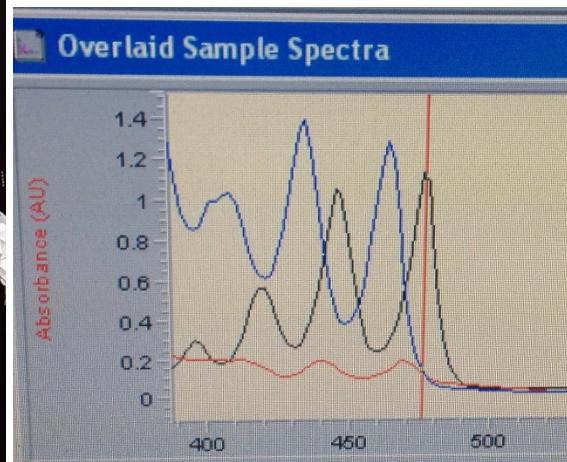


meanwhile, back in the
synthesis lab....

BT1 – Synthetic Platform



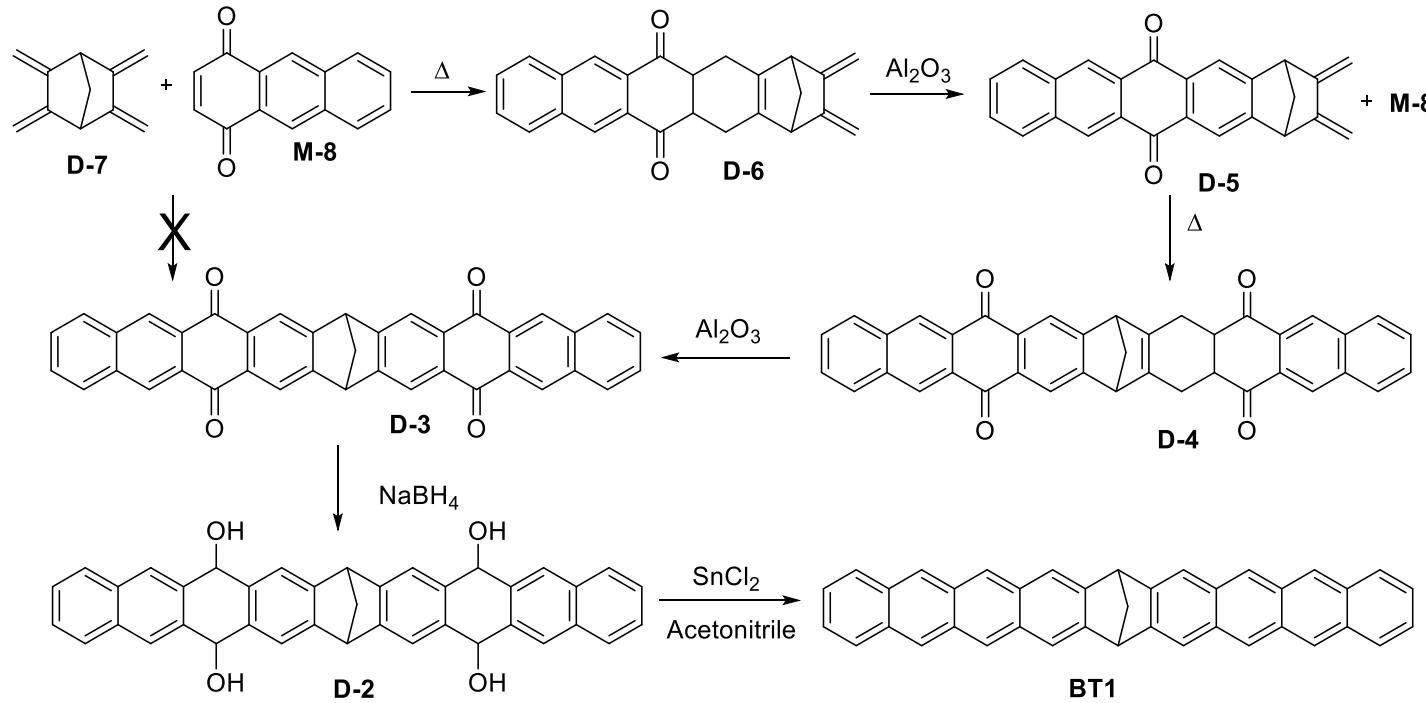
BT1 – Synthetic Platform



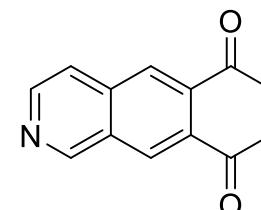
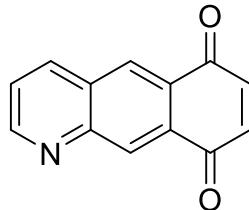
Breaking BT1 symmetry

Can we be synthetically smarter about it?

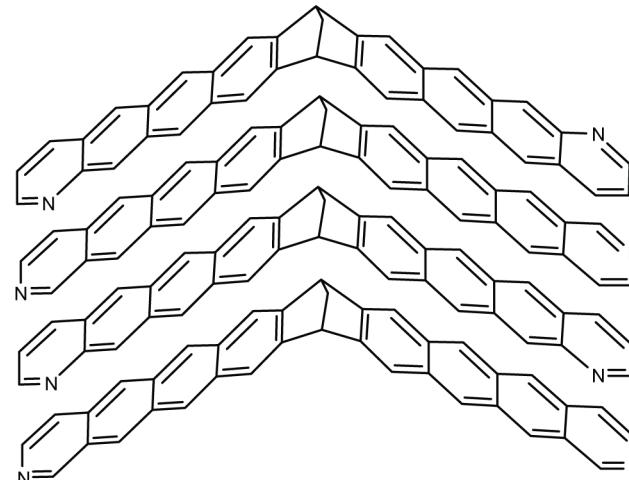
BT1 synthesis:



Heteroatom Substitutions:



Molecular Design – BT1-Aza



BT1-aza₁-C₂

BT1-aza₂-C₂

BT1-aza₁-C_s

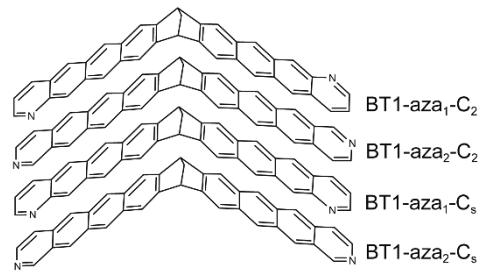
BT1-aza₂-C_s

Synthetic
design

Photophysics

Electronic Structure
Calculations

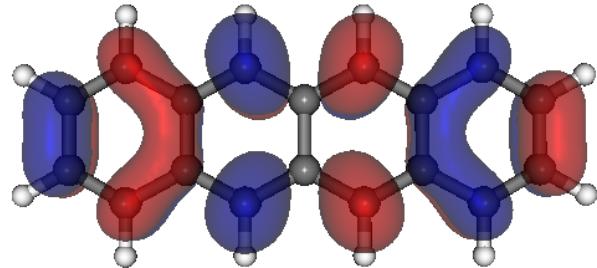
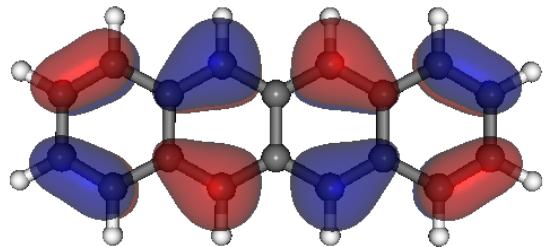
Frontier Orbitals



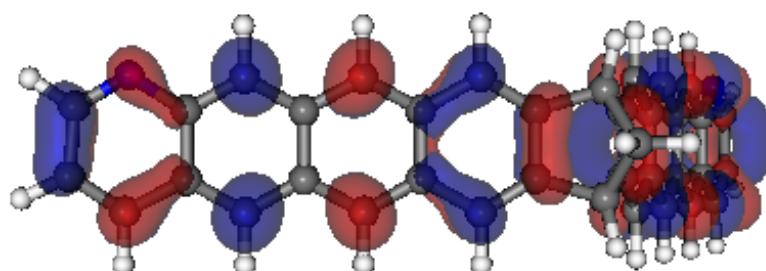
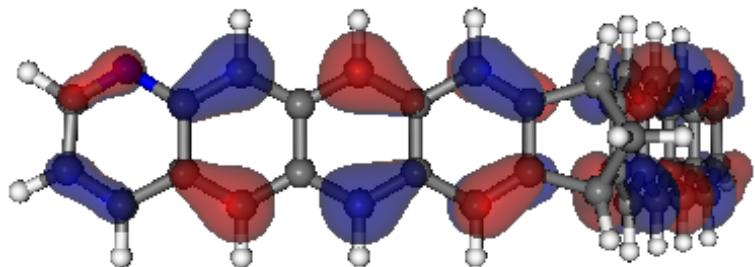
HOMO

LUMO

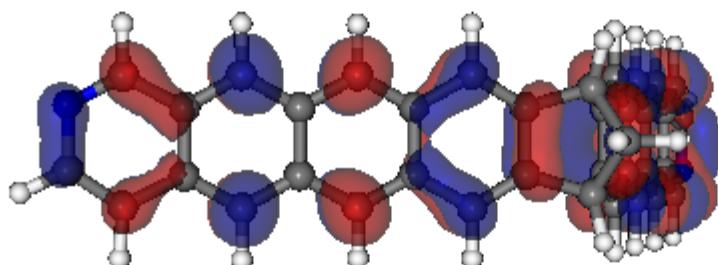
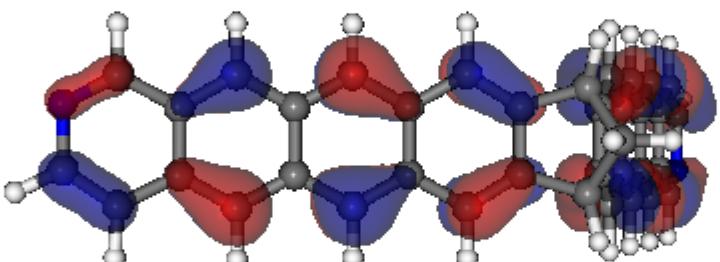
Tc



BT1-aza₁-C_s

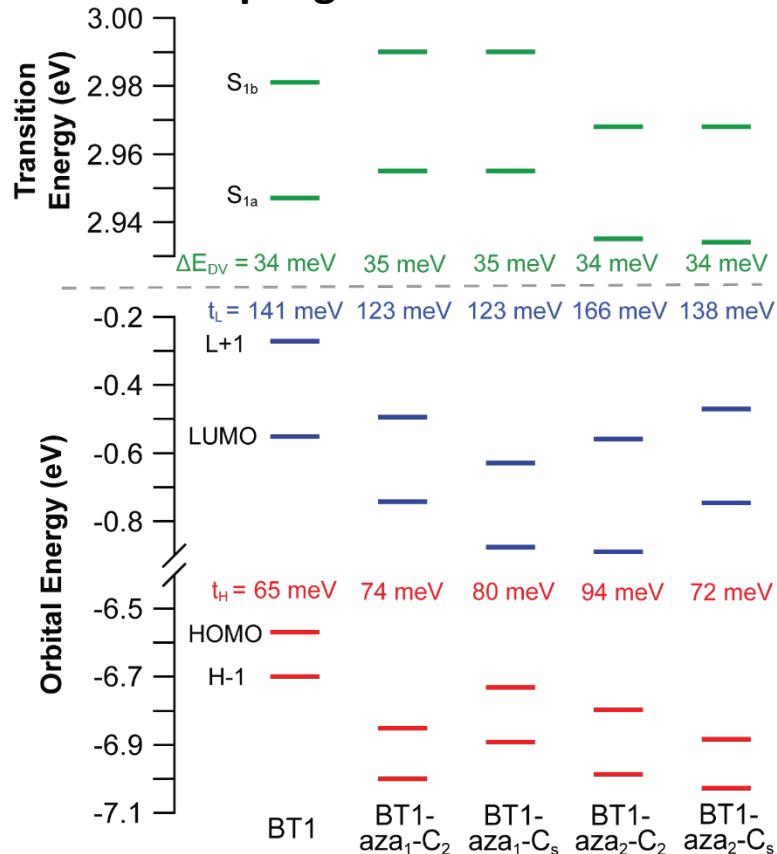


BT1-aza₂-C_s

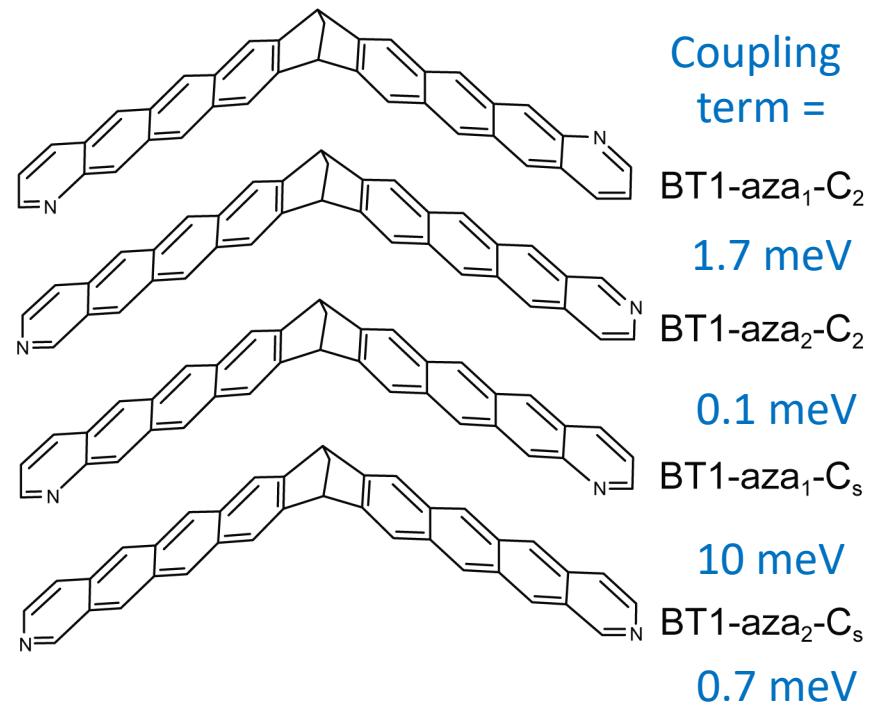


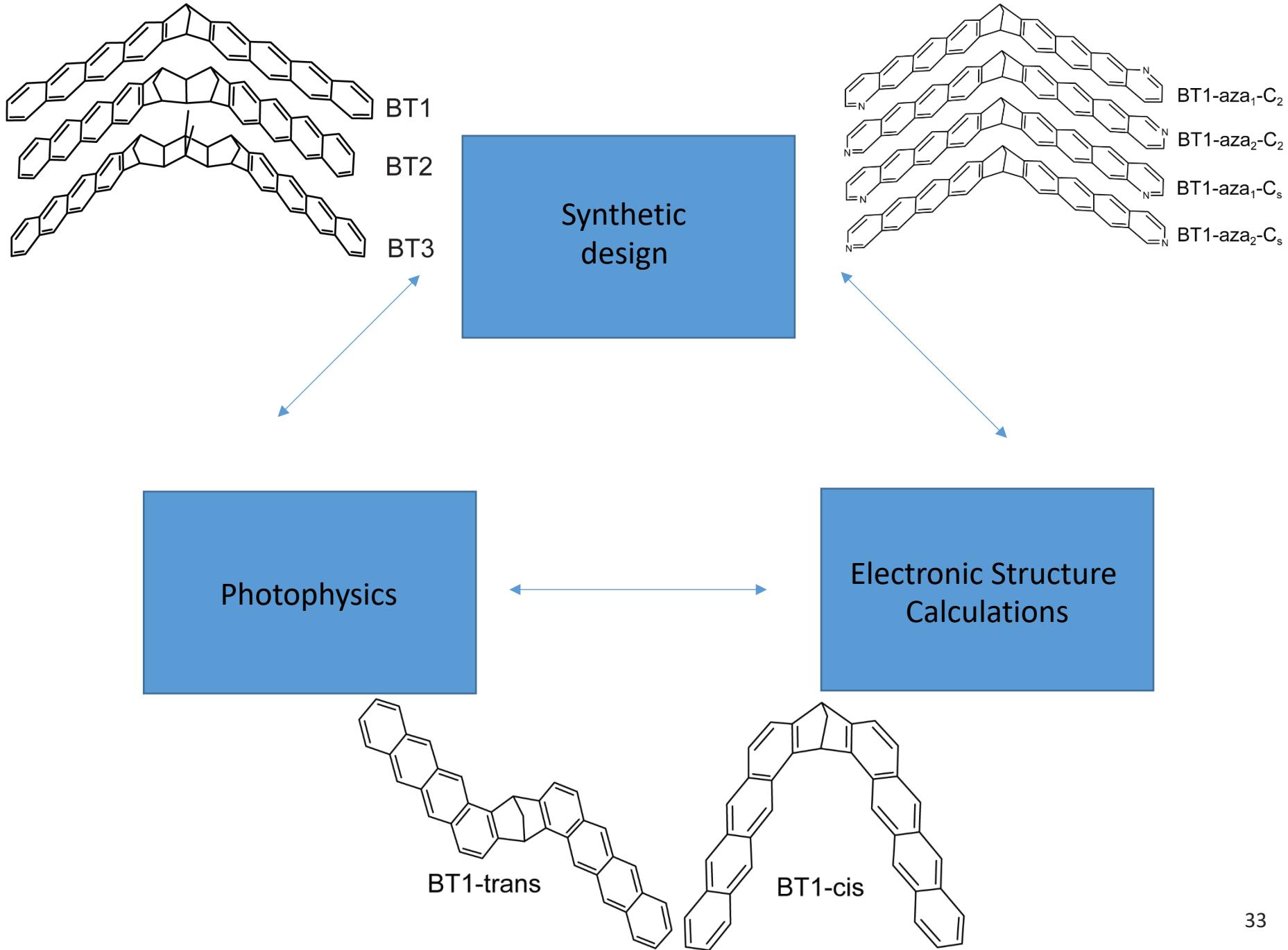
Communication in the Aza Series

Electronic Coupling



One-electron Coupling





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Sammakia Lab

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Teaching Staff

Chemistry Staff



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