

Excited-State Dynamics in DNA-Templated Molecular Dye Aggregates

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Acknowledgments

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Research:



INSPIRE
Award # 1648655

Specific equipment:



MRI
Award # 0923541
*Femtosecond laser
amplifier*

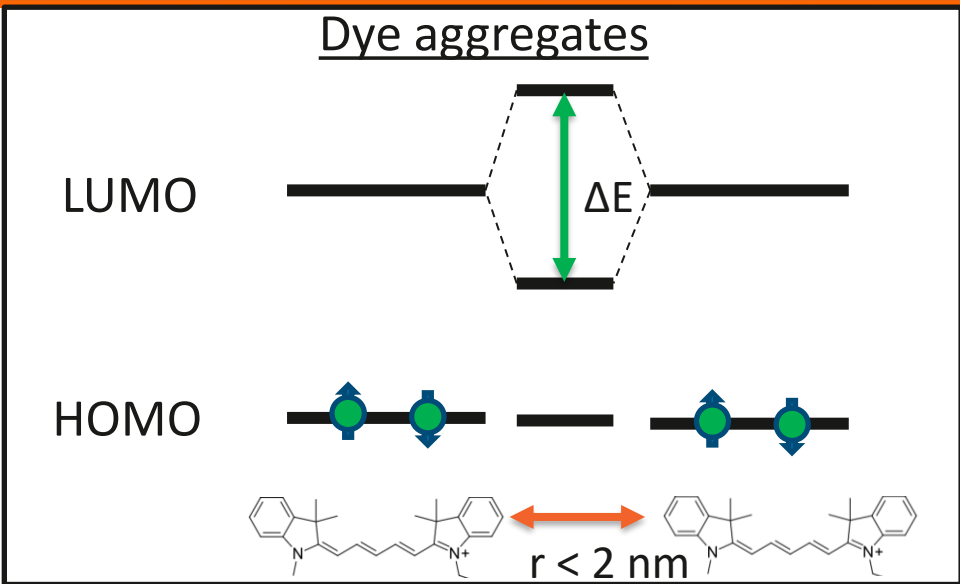


LDRD via contract # 154754
Femtosecond transient absorption
EPSCoR via award # DE-SC0020089
Steady-state circular dichroism



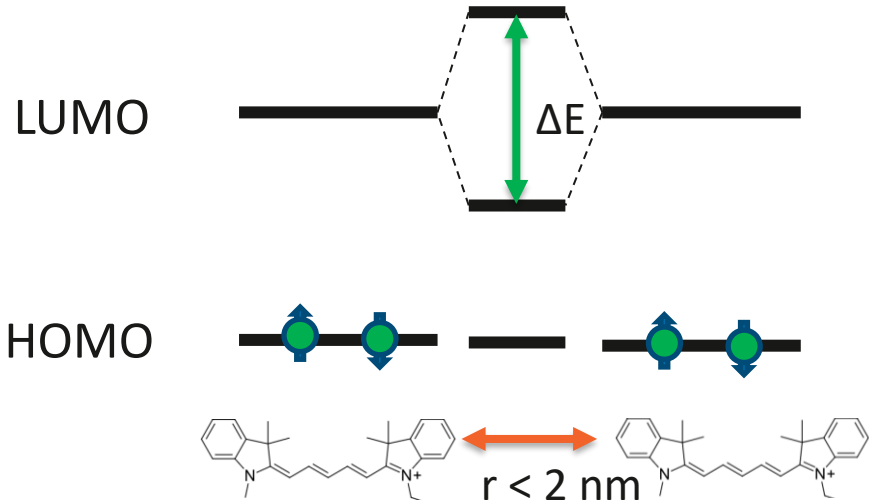
Award # N00014-19-1-2615
Picosecond fluorescence

Background and Motivation



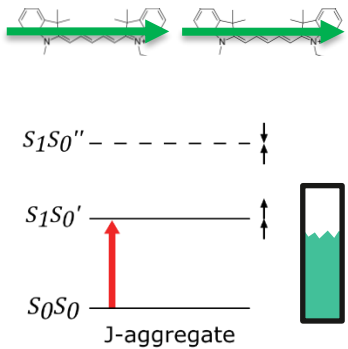
Background and Motivation

Dye aggregates

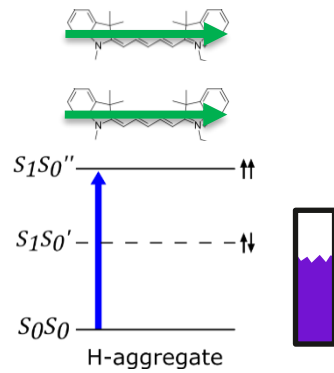


Dye packing dependence of properties

J-aggregate

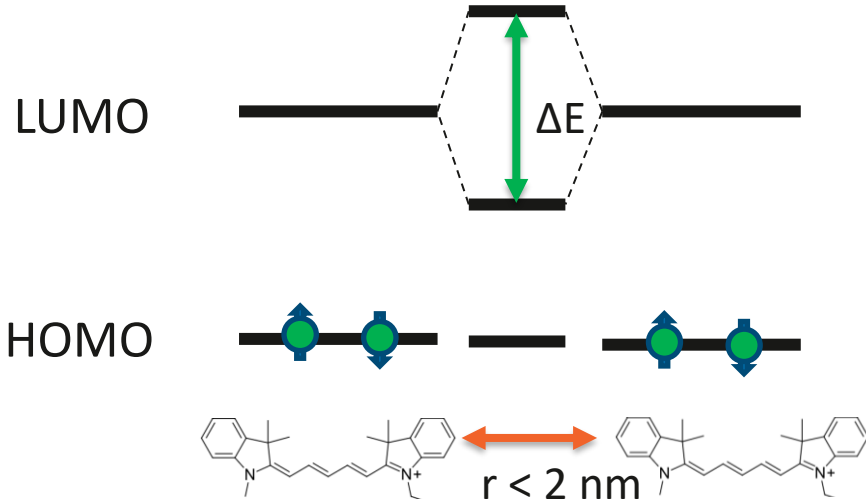


H-aggregate

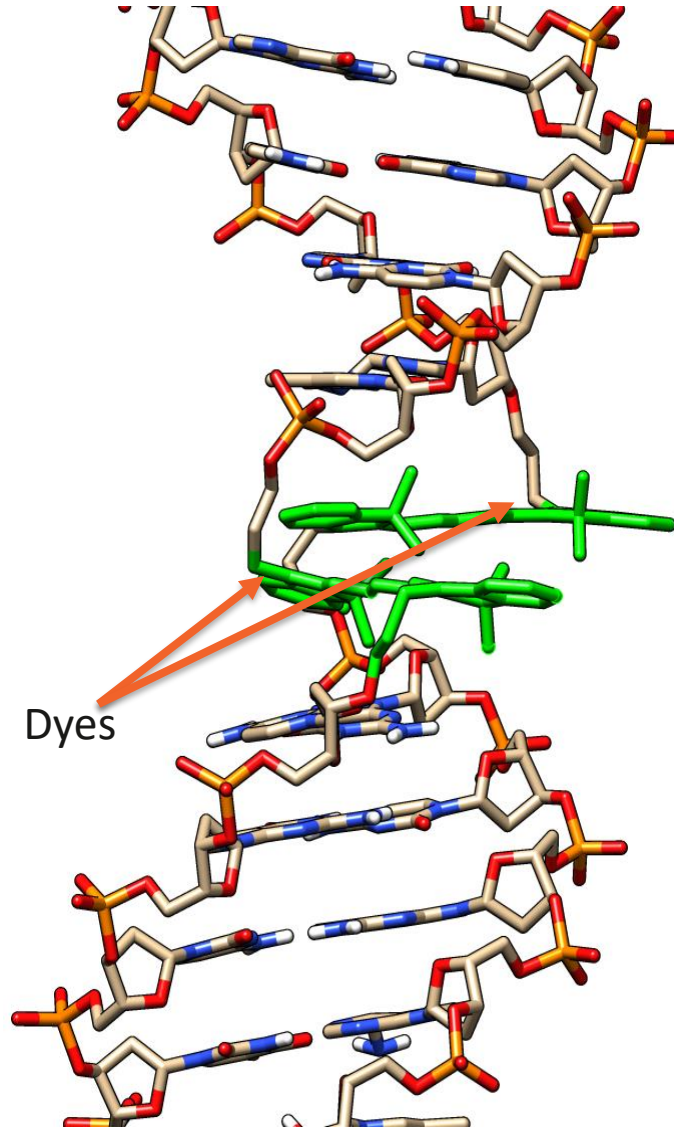


Background and Motivation

Dye aggregates

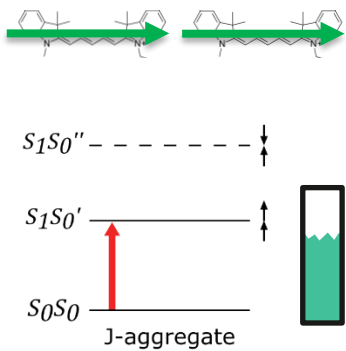


DNA as a scaffold for dye aggregates

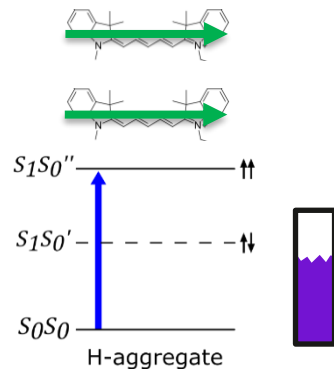


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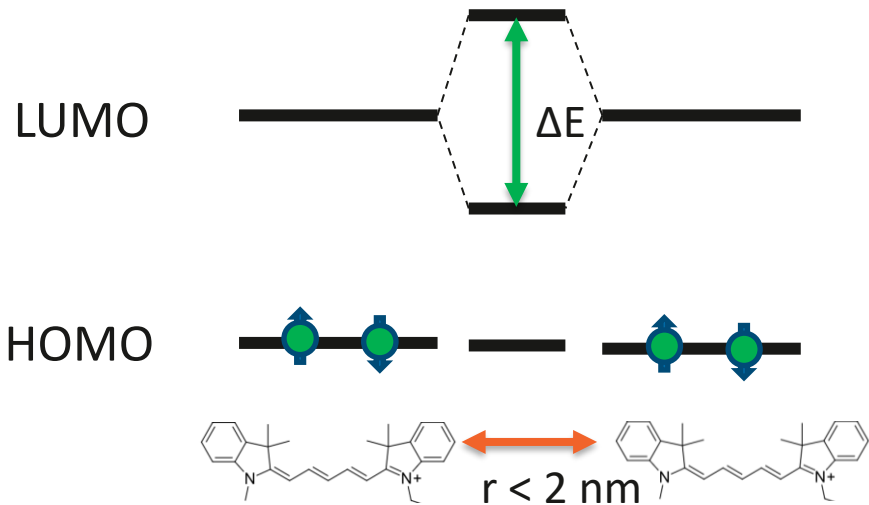


H-aggregate

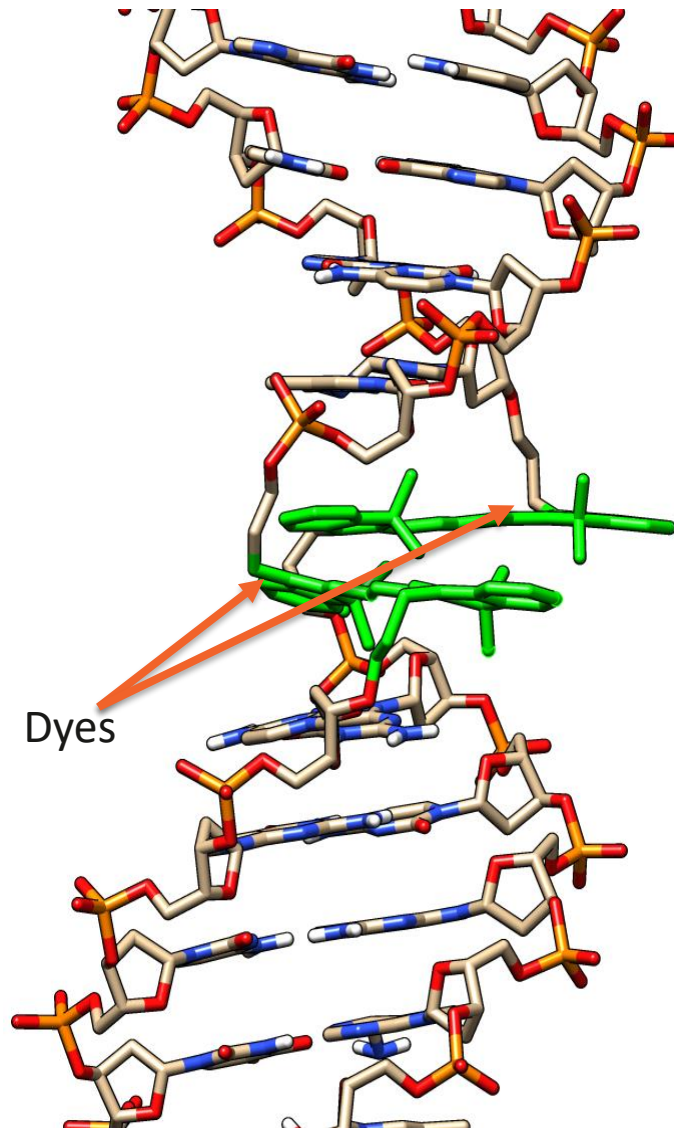


Background and Motivation

Dye aggregates

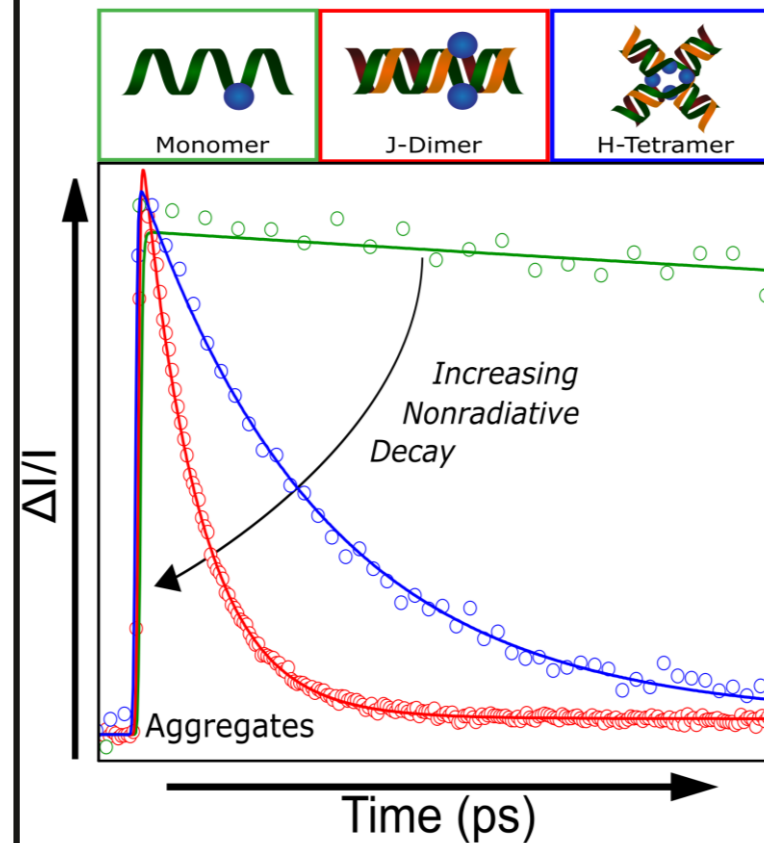


DNA as a scaffold for dye aggregates

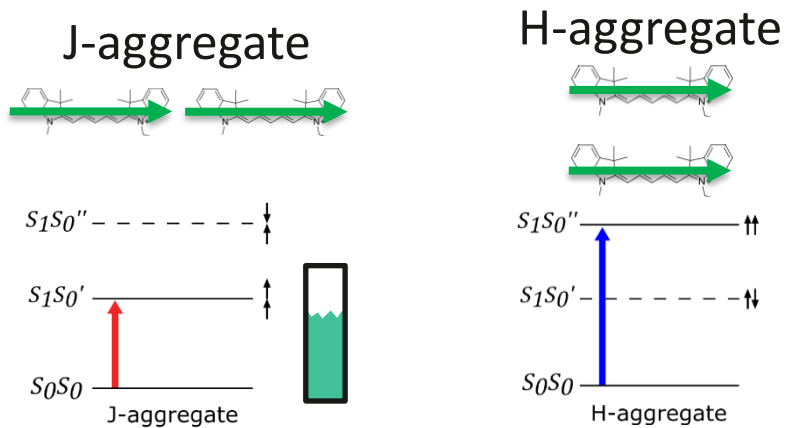


Excited state lifetimes

- Previously observed $\sim 35\text{-}100\times$ reduction compared to monomer [1]



Dye packing dependence of properties



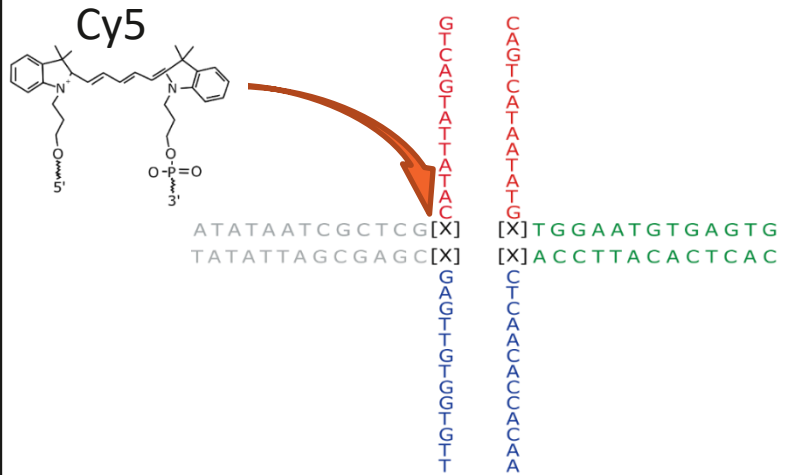
Key Knowledge Gap

How does the number of dyes in the aggregate influence nonradiative decay?

How does dye packing influence nonradiative decay?

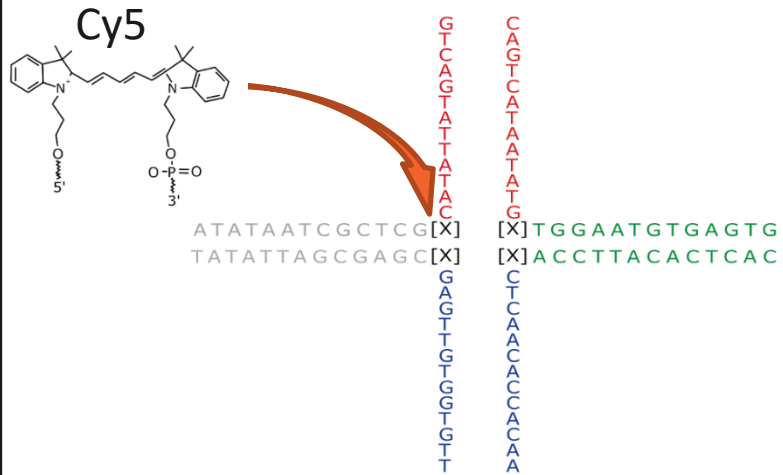
Results, Discussion, and Conclusion

Immobile DNA Holliday Junction Template



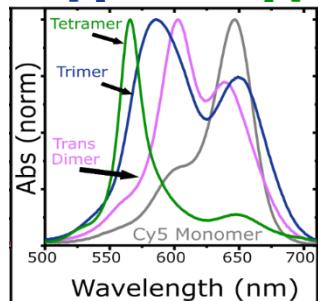
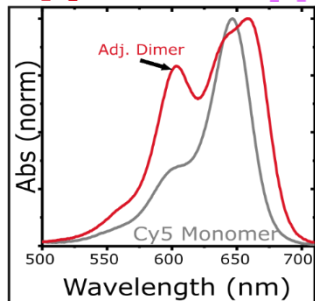
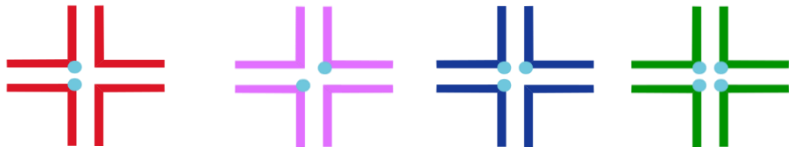
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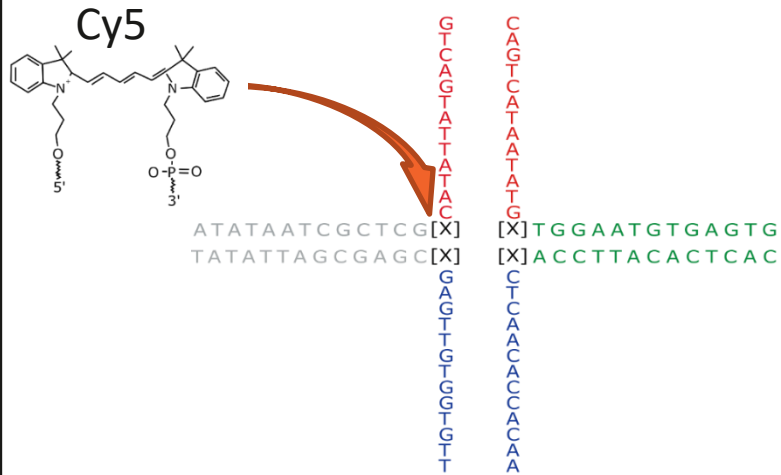
Immobile Holliday Junction Cy5 Aggregates

Adjacent Dimer Transverse Dimer Trimer Tetramer



Results, Discussion, and Conclusion

Immobile DNA Holliday Junction Template



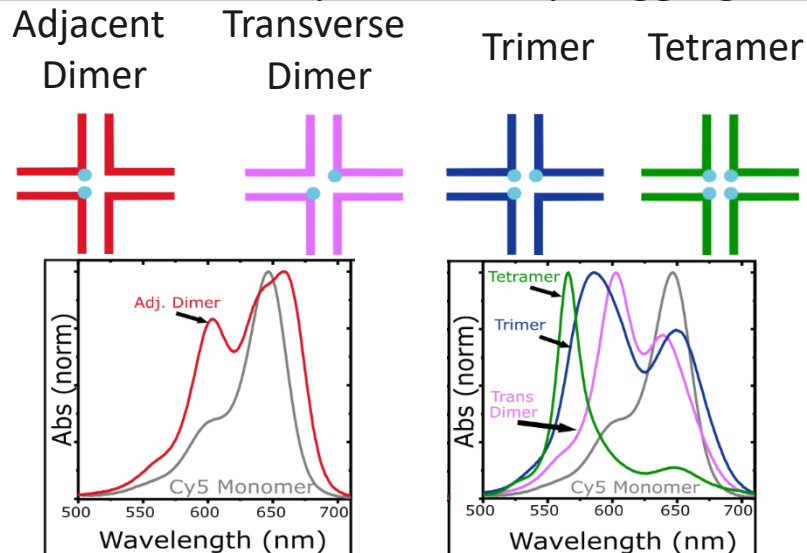
Excited-state dynamics

- Femtosecond transient absorption (TA) measurements showed all solutions exhibited complicated multiexponential relaxation dynamics.
- Additional TA measurements and global target analysis (GTA) revealed that the adjacent dimer and trimer solutions contain substantial aggregate subpopulations.

Solution	τ_1 (ps)	τ_2 (ps)
Monomer	1300	--
Adjacent Dimer	40	242
Transverse Dimer	202	--
Trimer	30	80
Tetramer	40	--

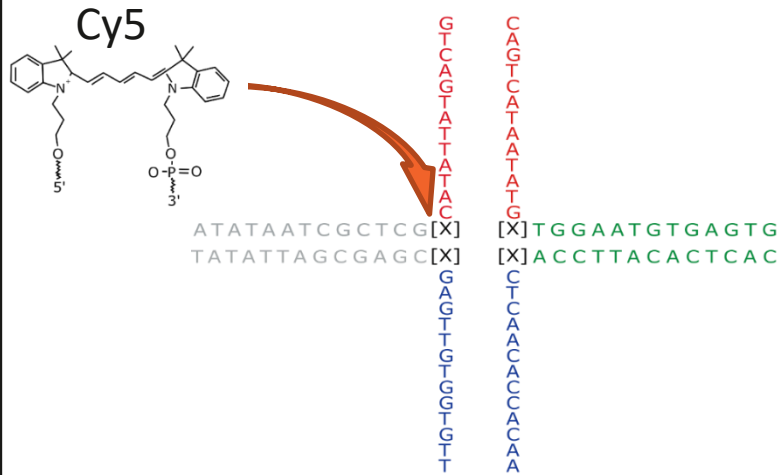
- All aggregate populations exhibit greatly reduced excited-state lifetimes due to increased nonradiative decay rate.

Immobile Holliday Junction Cy5 Aggregates



Results, Discussion, and Conclusion

Immobile DNA Holliday Junction Template



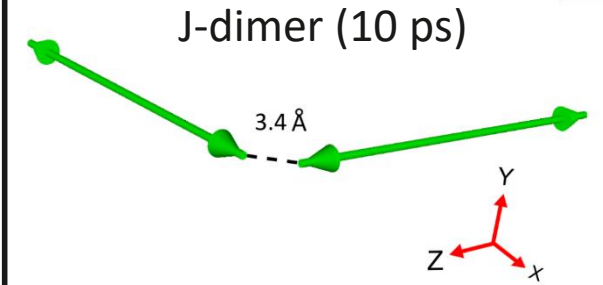
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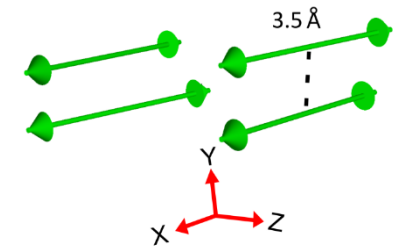
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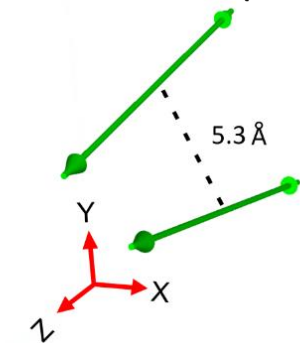
Proposed Mechanism



Immobilized HJ Tetramer (40 ps)



Transverse Dimer (202 ps)



Increasing dye separation and lifetime

Immobile Holliday Junction Cy5 Aggregates

Adjacent Dimer Transverse Dimer Trimer Tetramer

