# Excited-State Dynamics in DNA-Templated Molecular Dye Aggregates

*Jonathan S. Huff,[1] Daniel B. Turner,[1] Olga A. Mass,[1] Matthew S. Barclay,[1] Bernard Yurke,[1,2] William B. Knowlton,[1,2] Paul H. Davis,[1] Ryan D. Pensack[1,*]*

[1]Micron School of Materials Science & Engineering, and [2]Department of Electrical & Computer Engineering, Boise State University, Boise, Idaho 83725 *ryanpensack@boisestate.edu

## Acknowledgments

❖ We would like to thank Simon Roy and Lance K. Patton for their work modelling the aggregate structures

### Research:

INSPIRE
Award # 1648655

### Specific equipment:

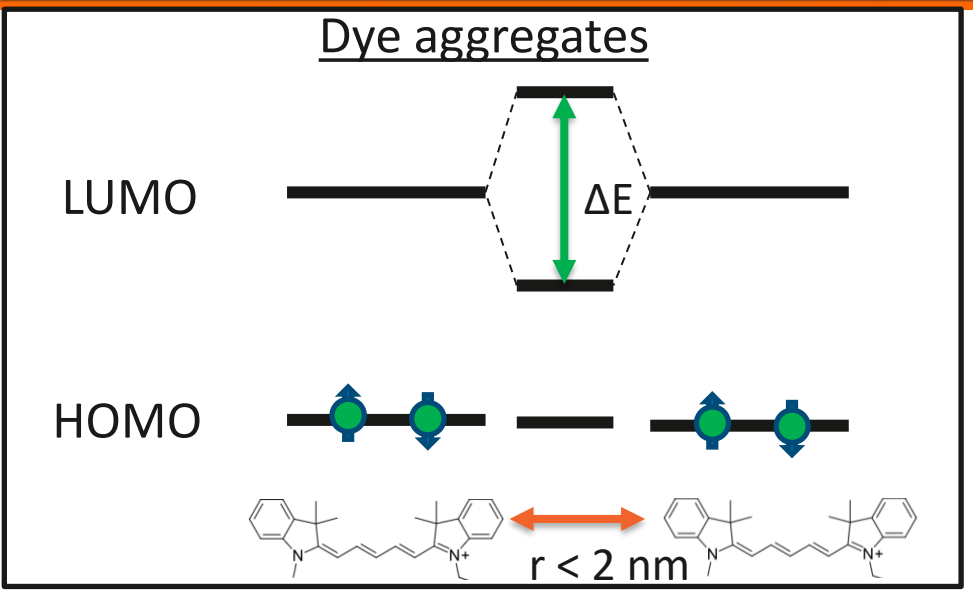
MRI
Award # 0923541
*Femtosecond laser amplifier*

LDRD via contract # 154754
*Femtosecond transient absorption*

EPSCoR via award # DE-SC0020089
*Steady-state circular dichroism*

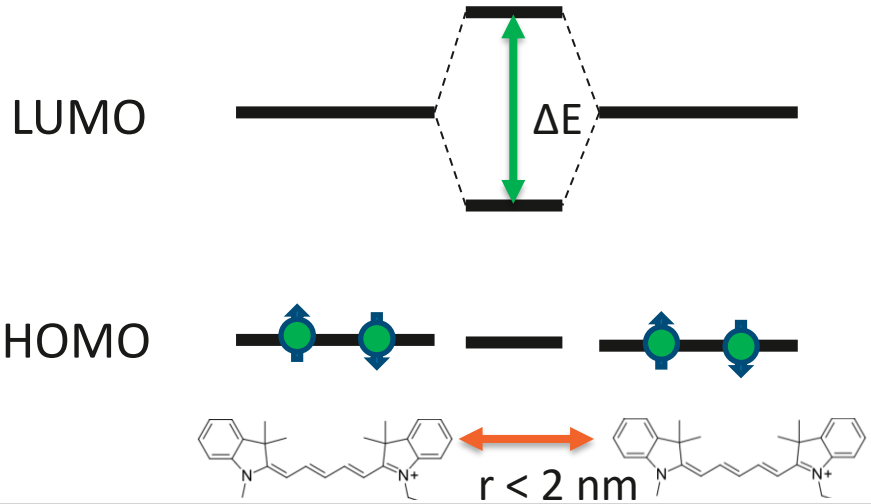
Award # N00014-19-1-2615
*Picosecond fluorescence*

# Background and Motivation

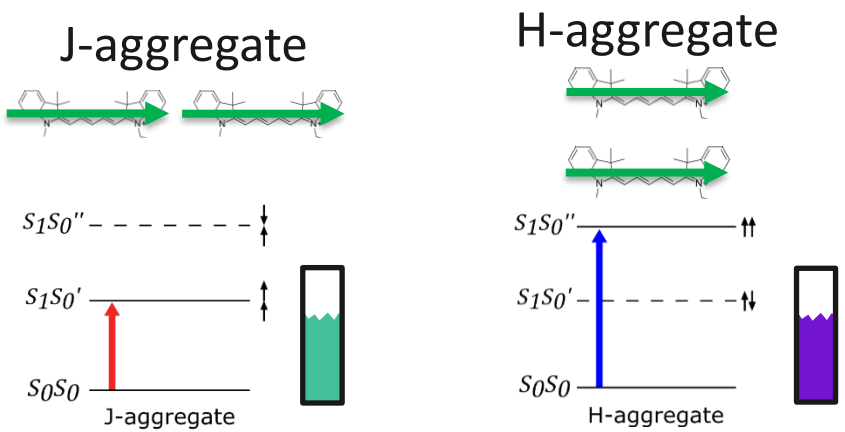


# Background and Motivation

## Dye aggregates

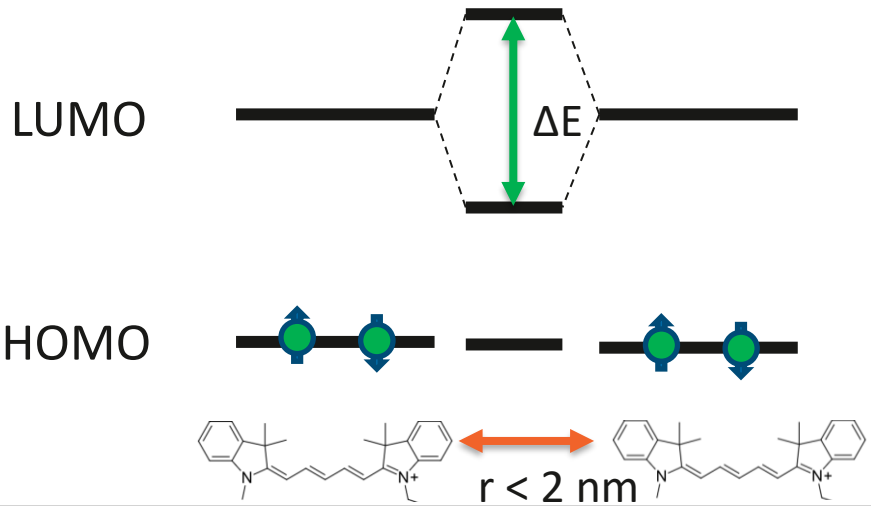



## Dye packing dependence of properties

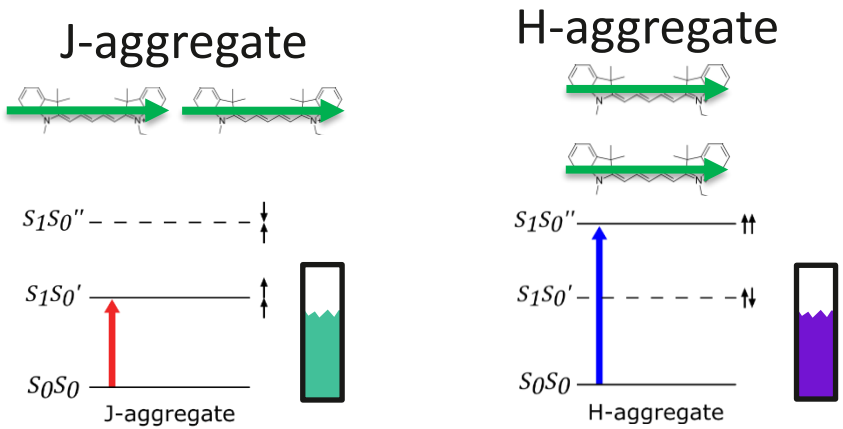


# Background and Motivation

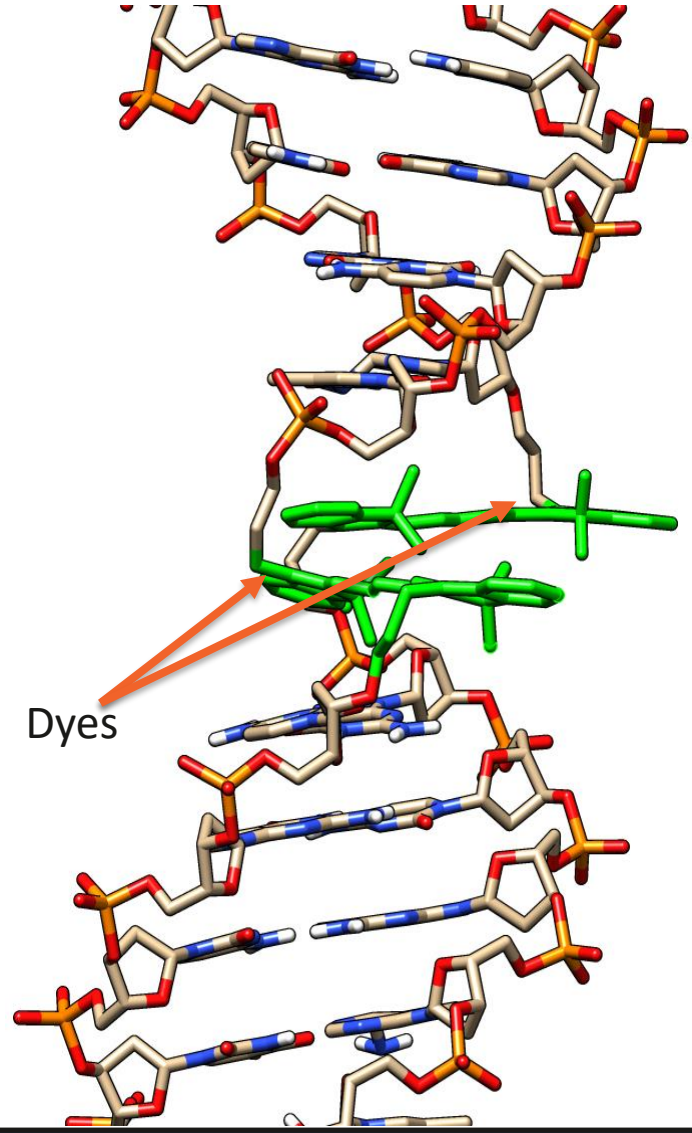
## Dye aggregates




## Dye packing dependence of properties

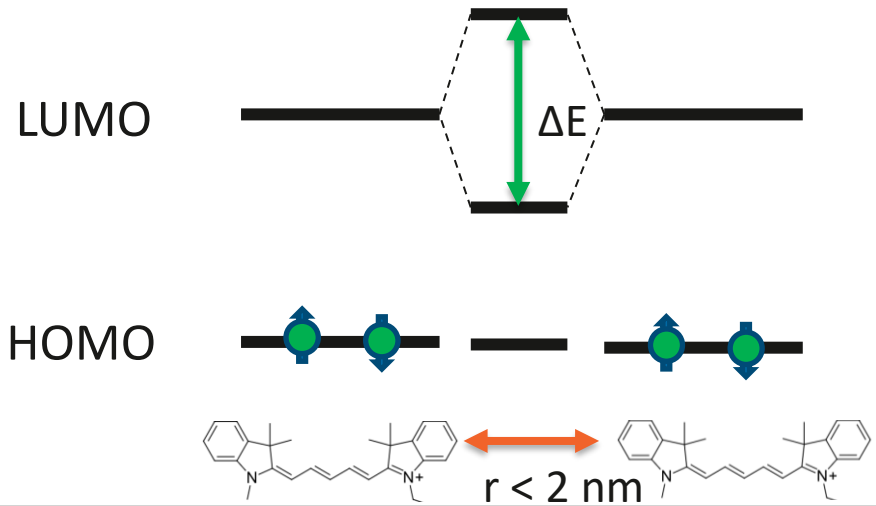



## DNA as a scaffold for dye aggregates

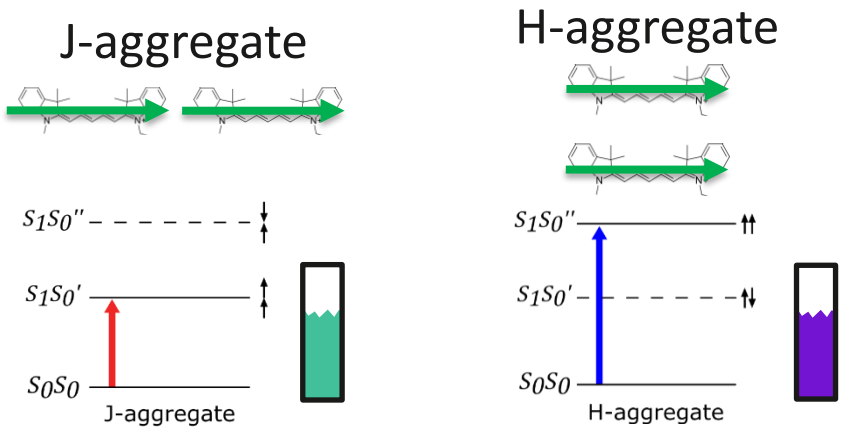


# Background and Motivation

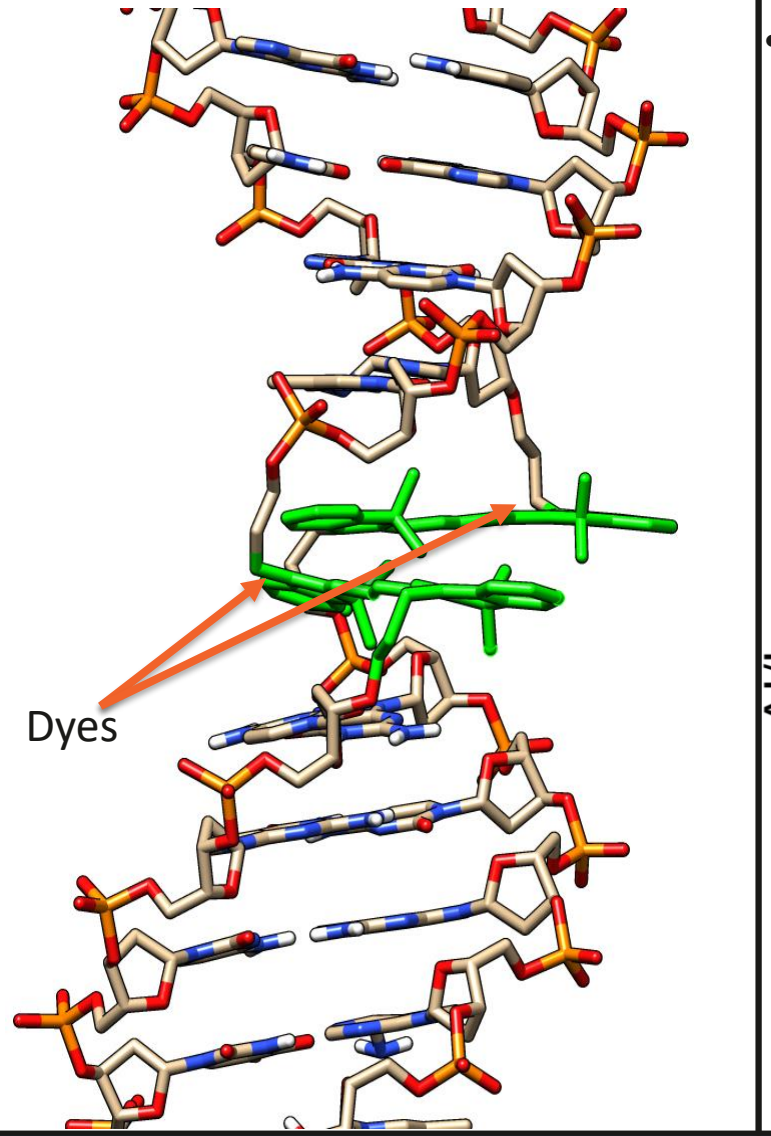
## Dye aggregates




## Dye packing dependence of properties

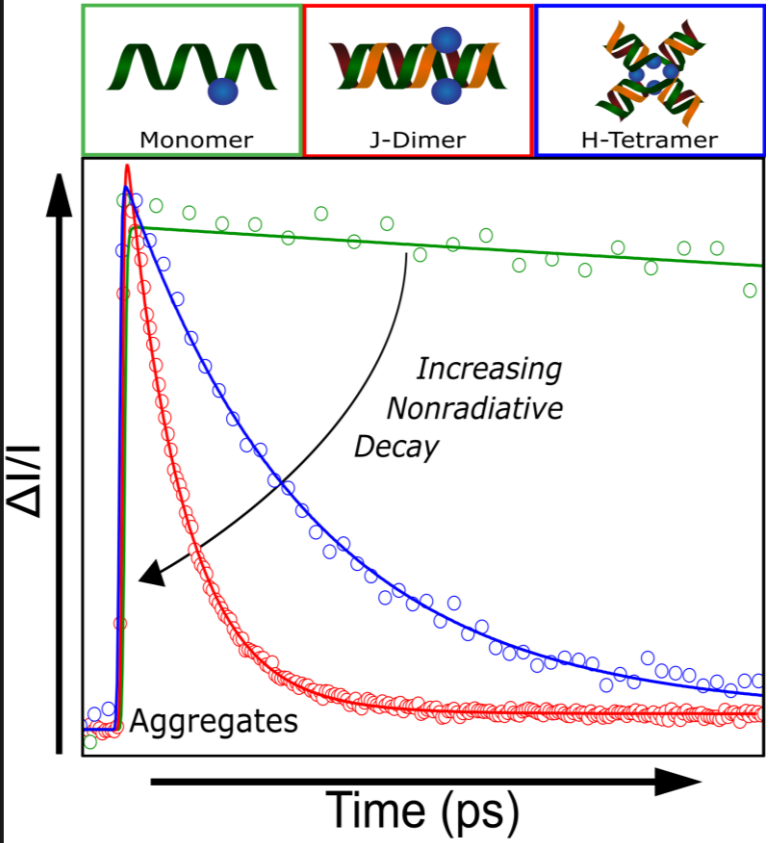



## DNA as a scaffold for dye aggregates




## Excited state lifetimes

- Previously observed ~35-100× reduction compared to monomer [1]






[1] J. S. Huff *et al., J. Phys. Chem. Lett.* **2019**, *10* (10), 2386.

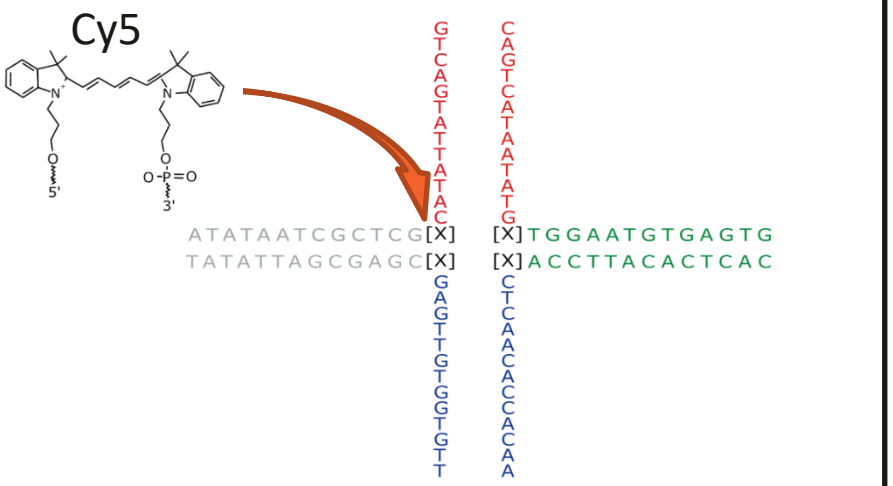
# Key Knowledge Gap

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

How does dye packing influence nonradiative decay?

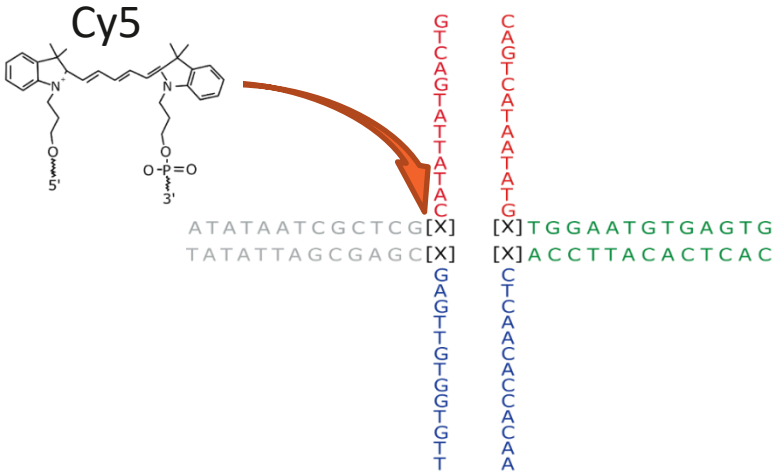
# Results, Discussion, and Conclusion

## Immobile DNA Holliday Junction Template

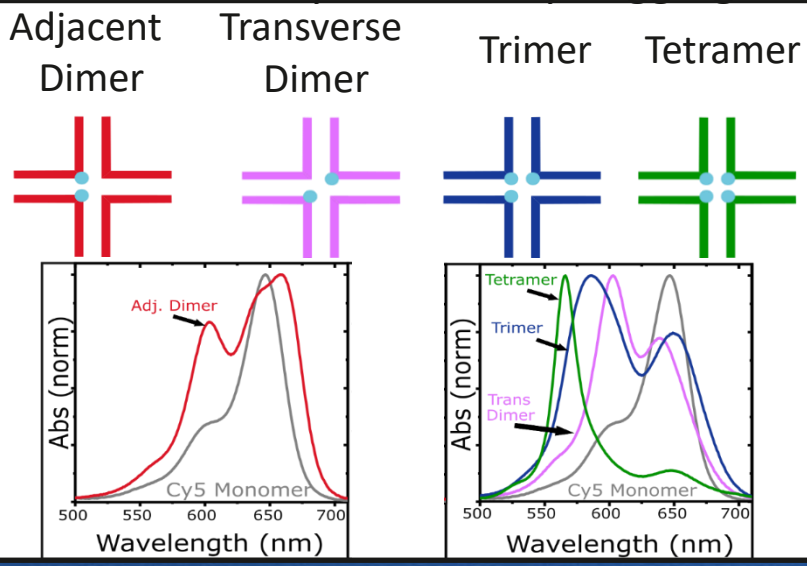


# Results, Discussion, and Conclusion

## Immobile DNA Holliday Junction Template

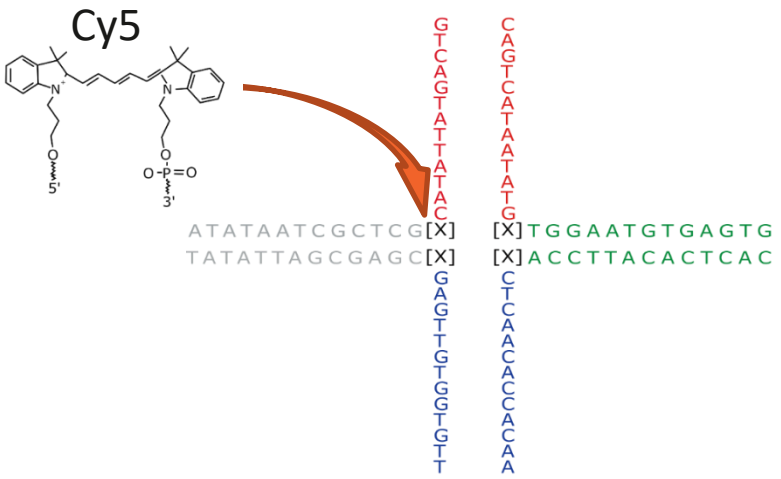



## Immobile Holliday Junction Cy5 Aggregates

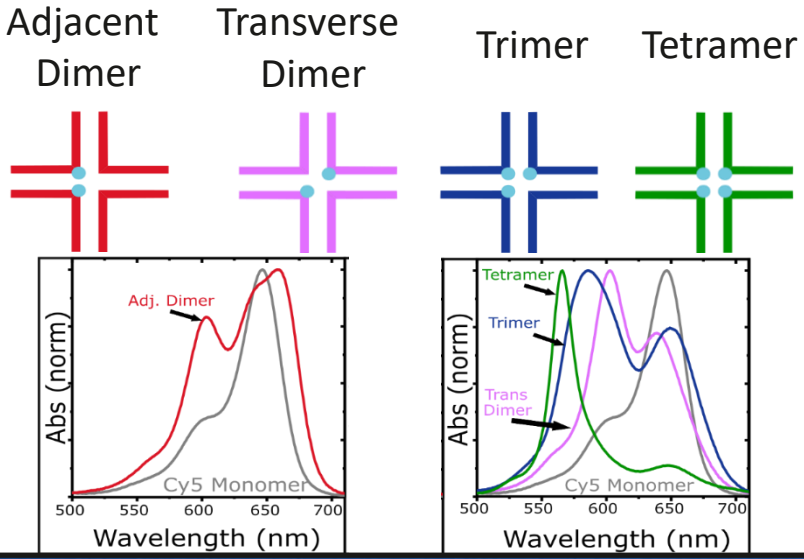


# Results, Discussion, and Conclusion

## Immobile DNA Holliday Junction Template




## Immobile Holliday Junction Cy5 Aggregates




## Excited-state dynamics

- Femtosecond transient absorption (TA) measurements showed all solutions exhibited complicated multiexponential relaxation dynamics.

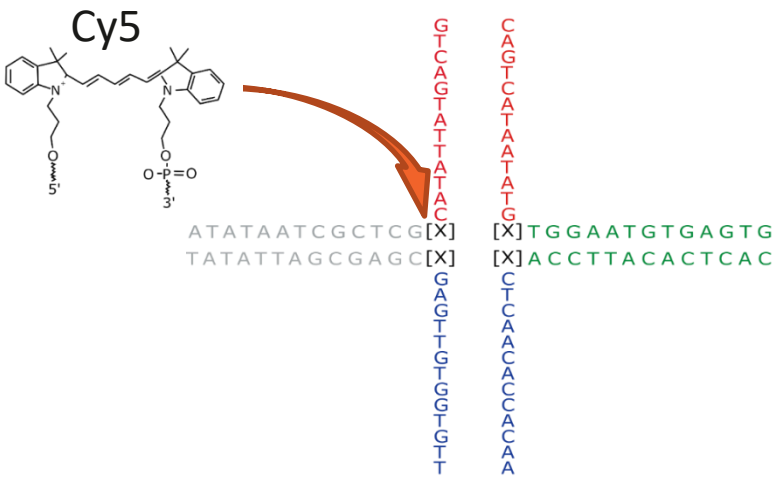
- Additional TA measurements and global target analysis (GTA) revealed that the adjacent dimer and trimer solutions contain substantial aggregate subpopulations.

| **Solution** | $\tau_1$(ps) | $\tau_2$(ps) |
|---|---|---|
| Monomer | 1300 | -- |
| Adjacent Dimer | 40 | 242 |
| Transverse Dimer | 202 | -- |
| Trimer | 30 | 80 |
| Tetramer | 40 | -- |

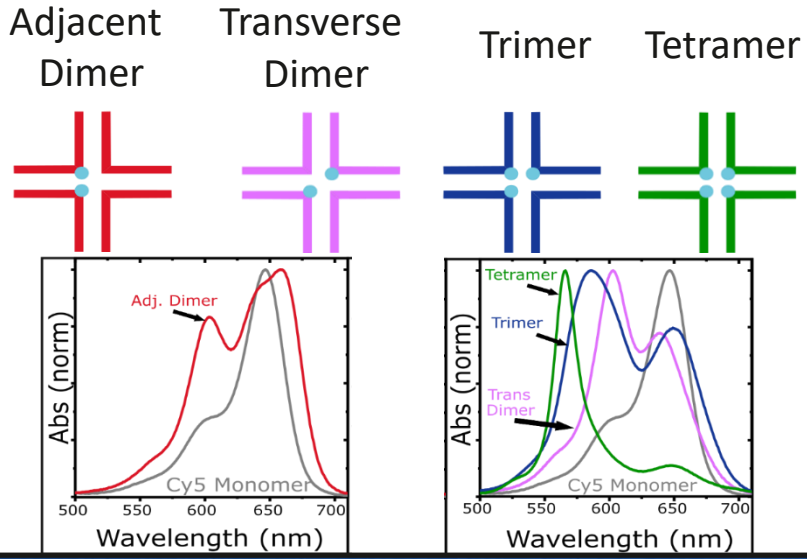
- All aggregate populations exhibit greatly reduced excited-state lifetimes due to increased nonradiative decay rate.

# Results, Discussion, and Conclusion

## Immobile DNA Holliday Junction Template




## Immobile Holliday Junction Cy5 Aggregates




## Excited-state dynamics

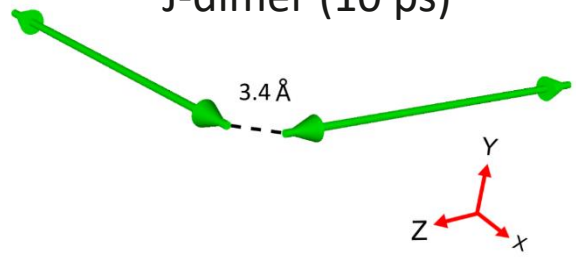
- Femtosecond transient absorption (TA) measurements showed all solutions exhibited complicated multiexponential relaxation dynamics.
- Additional TA measurements and global target analysis (GTA) revealed that the adjacent dimer and trimer solutions contain substantial aggregate subpopulations.

| Solution | $\tau_1$(ps) | $\tau_2$(ps) |
|---|---|---|
| Monomer | 1300 | -- |
| Adjacent Dimer | 40 | 242 |
| Transverse Dimer | 202 | -- |
| Trimer | 30 | 80 |
| Tetramer | 40 | -- |

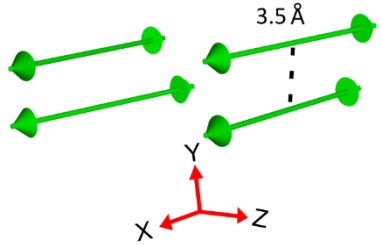
- All aggregate populations exhibit greatly reduced excited-state lifetimes due to increased nonradiative decay rate.

## Proposed Mechanism

J-dimer (10 ps)




Immob. HJ Tetramer (40 ps)




Transverse Dimer(202 ps)