DNA-Templated Cyanine Dye Aggregates: Nonradiative Decay Governs Exciton Lifetimes

Jonathan S. Huff,† Paul H. Davis,† Allison Christy,† Donald L. Kellis,† Nirmala Kandadai,‡ Zi S. D. Toa,§
Gregory D. Scholes,§ Bernard Yurke,*,†,‡ William B. Knowlton,*,†,‡ and Ryan D. Pensack*,†

†Micron School of Materials Science & Engineering and ‡Department of Electrical & Computer Engineering, Boise State University, Boise, Idaho 83725, United States

§Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

*(B.Y.) bernardyurke@boisestate.edu, *(W.B.K.) bknowlton@boisestate.edu, and *(R.D.P.) ryanpensack@boisestate.edu

1. Introduction & Motivation

Motivation & Background

- Excitons in molecular aggregates have sparked intense interest due to their potential applications in light harvesting (including natural, artificial, and biomimetic), organic optoelectronics and nanoscale computing.
- Dye aggregation was first reported in the 1930s when researchers observed marked changes in absorption spectra of concentrated cyanine dye solutions.[1–3]
- Figure 1 presents a summary schematic energy level diagram illustrating the excited-state band splitting and selection rules for the simplest type of dye aggregates—dimers.

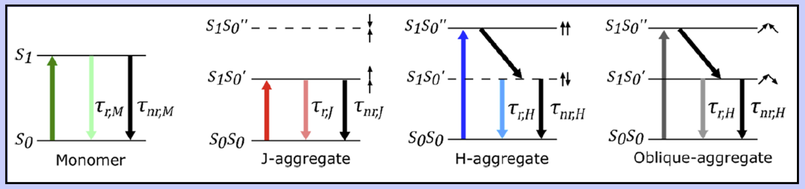
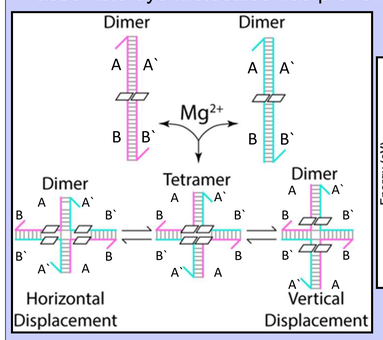


Figure 1. Schematic energy level diagrams of a dye monomer (far left), J-dimer (middle left), H-dimer (middle right), and oblique dimer (far right). A schematic representation of relative transition dipole moment orientations for each aggregate is shown to the right of each excitonic excited state. Solid horizontal lines indicate excitonic states that can couple optically to the ground state whereas dashed horizontal lines indicate excitonic states that cannot couple optically to the ground state. Optical transitions are shown as colored arrows for the monomer (green), J-aggregate (red), H-aggregate (blue), and oblique aggregate (gray). Optical (radiative) absorption is represented by dark colors, and optical (radiative) emission is represented by corresponding light colors. Nonradiative transitions are represented by black arrows. Reproduced from [9].

- While there are more advanced ways to control dye aggregation, such as using protein templates, using structurally less complex DNA oligonucleotides to assemble dye molecules has proven a more tractable approach.[4–9]



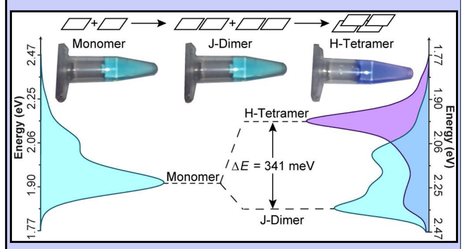
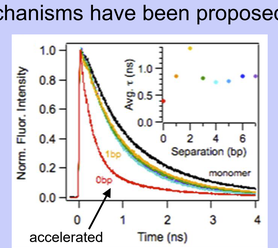
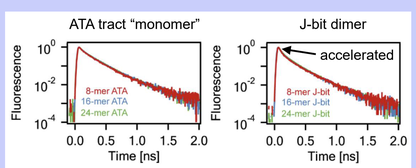


Figure 2. Top-Left Schematic illustration of how two J-dimers couple together at high salt/DNA concentration to form a Holliday junction and H-tetramer. Adapted from [4]. **Figure 2. Top-Right** shows absorption spectra (and vials) of the monomer, J-dimer, and H-tetramer prepared and characterized in ref. [4]. Both J-dimer and H-tetramer exhibit strong electronic coupling. Adapted from [4].

- Studies of excited-state dynamics in DNA-templated dye aggregates, which are critical to their application in excitonic devices, are unfortunately scarce. Accelerated decay kinetics are generally observed, and different decay mechanisms have been proposed to explain the accelerated decay kinetics.



Cunningham *et al.* [ref. 6] studied the excited-state dynamics of DNA-templated Cy3 dimers using transient absorption spectroscopy. These authors interpreted the accelerated decay kinetics to arise from enhanced nonradiative decay via photoisomerization.



Banal *et al.* [refs. 7,8] studied the excited-state dynamics of DNA-templated pseudoisocyanine dimers using time-resolved fluorescence. These authors interpreted the accelerated decay kinetics to result from enhanced radiative decay, i.e., superradiance, concomitant with aggregation.

- **Key Knowledge Gap**: Are accelerated lifetimes observed in DNA-templated molecular aggregates a result of radiative enhancement, nonradiative enhancement, or a combination of both?

2. Results & Discussion, Part A

FQY suggests nonradiative decay

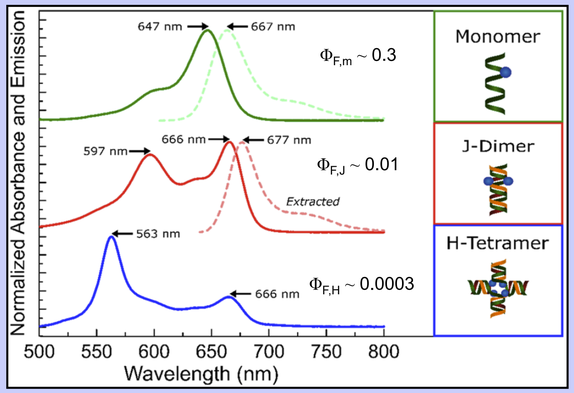


Figure 3. Steady-state absorption and fluorescence emission spectra with corresponding schematic illustrations for the DNA-templated Cy5 monomer (top), J-dimer (middle), and H-tetramer (bottom). The absorption spectra for the monomer, J-dimer, and H-tetramer are plotted in dark green, red, and blue, respectively, and the emission spectra for the monomer and J-dimer are plotted as dashed lines in light green and light red, respectively. The fluorescence emission spectrum of the J-dimer was extracted via the method described in our supporting poster. Due to a very low fluorescence quantum yield, it was not possible to extract the H-tetramer emission spectrum. Reproduced from [9].

- The steady-state absorption spectra compare very well with the group's literature precedent (ref. 4).
- Fluorescence emission was strongly quenched in the aggregate solutions
- A small sub-population of highly emissive monomers was found to contribute non-negligibly to the observed fluorescence emission of both PAGE-purified aggregate solutions. Thus, a procedure was developed to extract the "pure" emission spectrum of the aggregates.

Ps TRF confirms nonradiative decay

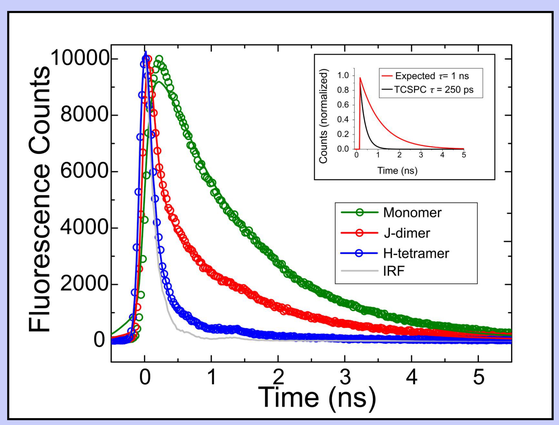


Figure 4. Time-resolved fluorescence decays of solutions of the monomer (green), J-dimer (red), and H-tetramer (blue). The instrument response function (IRF) is shown in solid gray. Open circles correspond to the experimental data, while the solid lines represent exponential decay fits convolved with the IRF. Inset: The observed (black trace) versus expected (red trace) fluorescence decays for the J-dimer. The expected decay assumes classical (Kasha-type) J-aggregate behavior, and that aggregation only affects the radiative decay rate (i.e., it assumes that $k_{nr,J} = k_{nr,m}$). For the purpose of illustrating the limiting case of full superradiance, it also assumes the maximum radiative rate possible, which for a dimer is $k_{r,J} = 2 \times k_{r,m}$. More details of the derivation are provided in our supporting poster. Reproduced from [9].

- While the monomer exhibits a lifetime of ca. 1.3 ns, the aggregates exhibit strongly accelerated fluorescence decays.
- The discrepancy between the expected (molecular exciton theory) and observed fluorescence decay kinetics indicates that new and significant nonradiative decay channels emerge in the aggregates.

3. Results & Discussion, Part B

Table 1. Excitation Wavelengths and Biexponential Fitting Parameters for TCSPC Decays[a]

construct	λ_{exc} (nm)	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)
monomer	653	N/A	1.3	N/A	N/A
J-dimer	653	87	≤ 0.25	13	1.3
H-tetramer	507	99.8	≤ 0.25	0.2	1.3

[a] The decays corresponding to the aggregate constructs were fit with the following biexponential function: $I(t) = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2}$. Additional details regarding the mathematical and physical justification of these biexponential fits can be found in our supporting poster.

Fs TA quantifies nonradiative decay

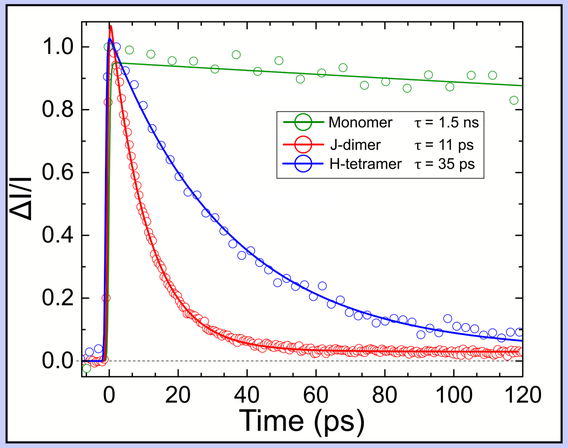


Figure 5. Transient absorption measurements on solutions of the monomer (green), J-dimer (red), and H-tetramer (blue). The open circles correspond to the experimental data, while the solid lines represent single or biexponential fits to the data. The data are scaled to unity. Reproduced from [9].

- The exciton lifetimes of the J-dimer and H-tetramer were measured to be ca. 11 and 35 ps, respectively.
- Estimating the k_r of the J-dimer and H-tetramer with experimentally available data (see our supporting poster for more details), nonradiative decay was determined to contribute 99.6% and >99.9%, respectively, to the overall decay.

4. Conclusion

In conclusion, we investigated the excited-state dynamics of strongly coupled J-dimer and H-tetramer constructs formed through covalent attachment of Cy5 to DNA. Quenched emission in steady-state fluorescence spectroscopy suggests that a new nonradiative decay pathway is introduced upon aggregation, which was confirmed via an analysis of TCSPC measurements in the context of molecular exciton theory. The exciton lifetimes of the J-dimer and H-tetramer were measured directly with transient absorption spectroscopy. Nonradiative decay was determined to be largely (>99%) responsible for the relaxation dynamics of both types of aggregates, which we attribute to a rapid nonadiabatic transition between S_1S_0 and S_0S_0.

5. References & Acknowledgments

References

[1] E.E. Jelley. Nature 1936, 138, 1009; **[2]** E.E. Jelley. Nature 1937, 139, 631; **[3] G.** Scheibe. Angew. Chem. 1937, 50, 212; **[4]** B.L. Cannon *et al.* J. Phys. Chem. A 2017, 121, 6905; **[5]** B.L. Cannon *et al.* J. Phys. Chem. A 2018, 122, 2086; **[6]** P.D. Cunningham *et al.* J. Phys. Chem. B 2018, 122, 5020; **[7]** Banal *et al.* J. Phys. Chem. Lett. 2017, 8, 5827; **[8]** J.L. Boulais *et al.* Nat. Mater. 2018, 17, 159; **[9]** J.H. Huff *et al.* J. Phys. Chem. Lett. 2019, 10, 2386.

Acknowledgments

Work at Boise State University was supported by the National Science Foundation (NSF), INSPIRE No. 1648655 and NSF MRI Award 0923541. Portions of this work were also supported by the Department of Energy (DOE), LDRD No. 154754. Z.S.D.T. and G.D.S. acknowledge support from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. DOE, through Grant No. DE-SC0019370.