

#### **BOISE STATE UNIVERSITY**

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### MOTIVATION

- Exciton delocalization in molecular (dye) aggregates governs progress in light harvesting, solar energy conversion, organic optoelectronics, and nanoscale computing.
- DNA template offers a very precise control over the number and position of dyes within a molecular aggregate
- An immobile 4-strand DNA Holliday Junction<sup>1</sup> (HJ) template allows creation of dye aggregates not achievable with dsDNA (e. g. adjacent dimer, trimer, tetramer).
- In our previous work, aggregates of Cy5 dye covalently templated via HJ<sup>2</sup> (Fig. 1a) exhibited some of the strongest excitonic hopping interactions observed among **Cy5** dye aggregates templated by DNA.<sup>3</sup>
- The use of Cy5 dyes is limited due to their photo instability and constraints in chemical structure manipulations.
- With optical properties similar to Cy5, indolenine squaraines<sup>4</sup> (SQ) exhibit increased photo stability, structural rigidity and structural diversity (Fig. 1b). Only one **SQ** dimer covalently templated by dsDNA was previously examined.<sup>5</sup>
- To quantitatively evaluate and compare the strength of excitonic hopping interactions that enable exciton delocalization between dyes in SQ versus Cy5 aggregates, here we applied a combination of molecular exciton theory, steady state optical characterization, and photophysical data analysis to extract excitonic hopping parameter  $J_{mn}$ .
- The work presented here has been recently published.<sup>6</sup>

### AGGREGATE DESIGN

Three types of squaraine-HJ aggregate configurations—transverse dimer, adjacent dimer, and tetramer-were created for comparison with previously reported cyanine-HJ transverse dimer and tetramer.<sup>2</sup> A single dye attached to HJ, i. e. a monomer, was used as a control (Fig. 1c).



Fig. 1. (a) Chemical structure of cyanine dye Cy5 with a dual phosphoramidite linker; (b) chemical structure of commercial indolenine squaraine Square-660 with a single linker for covalent attachment to DNA. (c) immobile DNA Holliday junction templating dye monomer, adjacent dimer, transverse dimer and a tetramer. The arms of DNA HJ are labeled A, B, C and D.

# **Exciton Delocalization in Squaraine Versus Cyanine Dye Aggregates Templated by DNA Holliday Junction**

### SPECTRAL SIGNATURES OF EXCITON DELOCALIZATION

Strong blue shift and Davydov splitting were observed in absorption spectra, and exciton-induced features were evident in CD spectra of SQ aggregates (Fig. 2) along with strongly suppressed fluorescence emission (not shown). These spectral changes were consistent with "H" or face-to-face packing and with strong exciton delocalization in all **SQ** aggregates. The theoretical spectra were obtained using the KRM modeling tool developed by our group to simultaneously fit the experimental absorption and CD spectra via Frenkel-Holstein Hamiltonian in which, following the theoretical approach of Kühn, Renger, and May,<sup>7</sup> the dominant vibrational mode is explicitly considered. A dye dipole was modeled as two-point charges of opposite sign separated by nearly the length of the dye core.



(bottom panel) Acquired CD spectra of the squaraine-HJ constructs (dotted lines), and theoretical CD spectra derived from KRM modeling (solid line). All samples were measured at 1.5 μM in 1×TBE, 15 mM MgCl<sub>2</sub> at room temperature.

#### DIMERS

The excitonic hopping parameter  $J_{1,2}$  quantifying excitonic interactions was obtained from the KRM modeling. The positions of dye transition dipole moments were extracted in terms of the zenith and azimuthal angles, and Cartesian coordinates from which a center-to-center distance, a slip angle, and an oblique angle were calculated (Fig. 3). Squaraine Cyanine



as Cy5 transverse dimer obtained by simultaneous modeling of experimental absorption and CD. Th models show  $J_{1,2}$  in meV, a center-to-center distance R in Å, a slip angle  $\theta_s^{\circ}$ , and an oblique angle  $\alpha^{\circ}$ .





### TETRAMERS

In the squaraine tetramer, three squaraine molecules were found to form an Hstack with a zigzag character while the fourth squaraine positioned out of the Hstack. The  $J_{m,n}$  ranged from 66 meV between two closest dyes to 2.8 meV between two furthest dyes (**Fig. 4**). In contrast, while  $J_{mn}$  between equidistant **SQ** dyes and Cy5 dyes are comparable, all four Cy5 dyes are proximate within a Hstacked parallelogram-like arrangement. The difference in the geometries of SQ and Cy5 tetramers might be due to the nature of the linkers tethering the dyes to DNA (**Fig. 1**).

**Squaraine tetramer** 

**Cyanine tetramer** 



Fig. 4. Molecular models of the indolenine squaraine Square-660 tetramer and Cy5 tetramer obtained by simultaneous modeling of experimental absorption and CD. The models show  $J_{m,n}$  in meV, a center-to-center distance R in Å , a slip angle  $heta_{
m s}$  °, and an oblique angle lpha °.

### SIGNIFICANCE AND MPACT

- We show that exciton delocalization occurs in DNA-template aggregates of SQ dyes, which absorb visible light strongly and are highly structurally tunable. Based on theoretical modeling, SQ and Cy5 aggregates exhibit comparable
- strong excitonic delocalization indicative from the relatively large excitonic hopping  $(J_{1,2})$  values of 65–70 meV.
- The **SQ** dye aggregate displayed primarily H-like stacking in all the aggregates examined versus mainly H-like with some J-like stacking<sup>2</sup> in Cy5 dye aggregates.
- Our findings and superior photophysical properties of SQ dyes over that of cyanine dyes make **SQ** dye aggregates very attractive candidates for molecular exciton-based applications.
- The key to advancing the field is the development of design strategies based on dye packing, to promote either or both J-like and H-like stacking.

## ACKNOWLEDGMENT & REFERENCES

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