

Potential Energy

Weaving DNA strands to control energy

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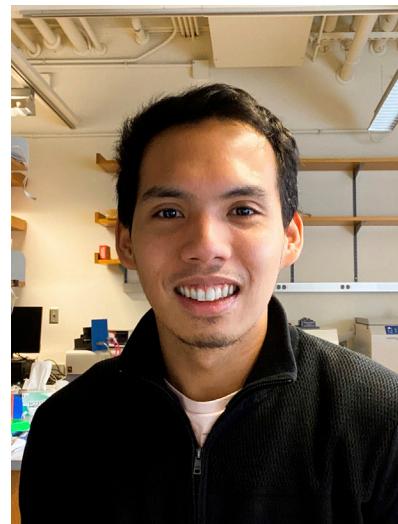
Dr. James L. Banal is currently a postdoctoral research associate in the Department of Biological Engineering at the Massachusetts Institute of Technology, where he works on engineering excitonic materials and molecular data storage using DNA. He obtained his PhD in 2016 at the University of Melbourne, where he studied the photophysics of molecular aggregates in luminescent solar concentrators. His research interests lie at the intersection of materials chemistry, optical spectroscopy, and engineering of optoelectronic devices.

Watson-Crick base pairing of DNA has provided a powerful paradigm for constructing structurally precise nanomaterials via self-assembly. Recent advances in automated algorithms for DNA origami to optimally route a long single-stranded DNA scaffold across the desired geometry and select short single-stranded DNA staples to maintain the desired shape have enabled the realization of arbitrarily complex 2D and 3D nanostructures.¹ Developing approaches that would allow for programmed assembly of secondary molecules on the DNA nanostructure is a critical next step for engendering synthetic function into these designer nanomaterials to develop the next generation of molecular devices.

One potential research field where synthetic programmable scaffolds can be an enabling tool is in the area of excitonic materials, wherein precise control over the energy, lifetime, and position of molecules in devices is essential to achieving the desired creation, transport, and, in some cases, annihilation or recombination of excited states across a range of length scales. Detailed investigation of the photophysics of excitonic materials, such as organic chromophores, is encumbered by the fact that most samples are often inhomogeneous, i.e., they are commonly polydispersed in size, and their structures are often disordered.²

Structural disorder obscures important insights that we can use to design better excitonic materials and pose a challenge to their integration in devices. My colleagues and I sought to address this challenge by using DNA as scaffolds to control the spatial relationship between chromophores. In a recent example, we studied an approach wherein superradiant aggregates of pseudoisocyanine were spatially controlled by specific DNA sequences. This approach offered the ability to investigate how aggregates can be used to steer energy toward the desired processes.^{3,4} However, inhomogeneous binding of pseudoisocyanine on the DNA minor groove³ hindered our attempts to understand the role of both the molecular aggregates and the DNA scaffolds in energy transfer, which prompted us to seek alternative covalent approaches. In this issue of *Chem*, we describe a synthetic strategy that introduces the ability to discretely control the intermolecular electronic coupling of molecular aggregates and their interaction with their DNA environment.⁵

Using phosphoramidite chemistry, we demonstrated the covalent attachment of one, two, and three Cy3 chromophores consecutively on a single DNA strand to synthesize a Cy3 monomer, dimer, and trimer, respectively, which contrasts existing strategies that rely instead on the hybridization of comple-



mentary dye-modified DNA strands to form aggregates. Given synthetic challenges in precisely attaching secondary molecules on the long DNA scaffold of larger DNA origami structures, our chosen synthetic strategy was initially conceived to circumvent the need to modify the complementary strand to create Cy3 aggregates. Our synthetic approach also offers the ability to program the electronic structure of strongly coupled Cy3 dimers discretely by using nucleotide spacers on DNA duplexes, which results in Cy3 dimers with varying degrees of electronic coupling (Figure 1). By limiting the formation of aggregates on a single strand, our synthetic design permits modular assembly of Cy3 monomer- or dimer-modified strands into double-crossover (DX) DNA tiles without perturbing the electronic structure of the Cy3 dimer and maintaining strong electronic coupling. Beyond these technical achievements, the ease of switching scaffolds from DNA duplexes and DX tiles without affecting the

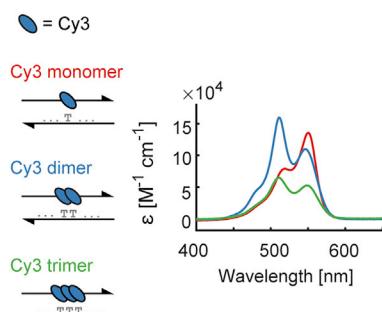
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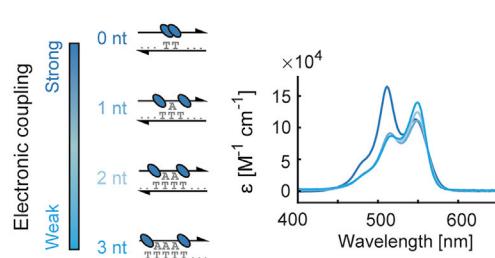
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Controlling number of aggregates



Controlling electronic coupling strength



Controlling energy transfer

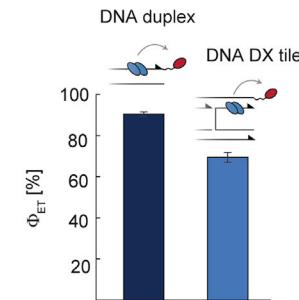


Figure 1. Controlling the photophysics of aggregates by using covalent attachment of dyes on DNA scaffolds. Error bars represent standard deviations calculated from three independent replicate measurements.

dimer's electronic structure enabled us to unravel the influence of the DNA on the photophysics of Cy3 at the femtosecond and nanosecond timescales by using ensemble 2D electronic and single-molecule fluorescence spectroscopy (see the accompanying viewpoints from the co-first authors in this issue's other Potential Energy articles). Using a joint experimental and computational approach, we developed a molecular mechanism on how the DNA scaffold plays a critical role in energy transport.

Although we don't anticipate these DNA-scaffolded dyes to replace the active materials on solar cells and light-emitting displays anytime soon, the advances we have shown here provide a path to gaining a microscopic understanding of exciton generation, transport, and conversion. These DNA-scaffolded materials can function as model systems—a tractable molecular toy model that can be fabricated and reconfigured via DNA self-assembly—

that theorists and experimentalists alike can explore with existing tools to answer open questions in exciton science, e.g., what is the influence of strongly coupled systems in energy transport? Extension of our work could seek to incorporate aggregates with emergent photophysics that leverage other excitonic properties, e.g., spin, which would enable the fabrication of a gamut of well-defined bespoke "parts" that could be assembled on the DNA origami "breadboard." Similarly to how the synthetic biology revolution began with identifying well-defined biological "parts" to imbue genetic circuits with synthetic function, the convergence of engineering principles and designer nanoscale excitonic circuits could lead to the discovery of new devices with yet-to-be-known operational characteristics. The ability to program the electronic structure of materials and their nanoscale organization by using DNA nanotechnology moves us closer to weaving designer molecular devices that rival and, hope-

fully one day, supersede inorganic semiconductor materials in computing, sensing, and energy conversion.

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