Watching DNA nanotechnology at the speed of light

Stephanie M. Hart[1,*]

Stephanie M. Hart is currently a National Science Foundation graduate research fellow at the Massachusetts Institute of Technology Department of Chemistry, where she is conducting her doctoral research in the lab of Prof. Gabriela Schlau-Cohen. She obtained her bachelor's degree in chemical engineering from the University of Minnesota in 2017. Her research interests pertain to the ultrafast spatiotemporal dynamics of energy transfer, delocalization, and charge transfer in condensed-phase systems.

Light-driven photophysical and photochemical transformations are key phenomena underlying numerous processes, including photosynthesis, vision, and photovoltaic light harvesting. The development of mode-locked femtosecond lasers has revolutionized the way that chemists think about light interactions with molecular systems. Utilizing coherent pulses of light can allow direct observation of photophysical processes such as exciton transport, vibrational motion, and electron transfer on their characteristic timescales, ranging from femtoseconds to picoseconds, via ultrafast spectroscopy.

Natural photosynthetic systems such as plants, algae, and bacteria use nanoscale arrangements of biological chromophores to harvest light with near-unity quantum efficiency on the femtosecond to picosecond timescale.[1] Ultrafast spectroscopy has been used to unravel the dynamics associated with this transport process in biological systems with varying structural motifs. From these studies, design principles that can be emulated in synthetic systems have emerged.[2] However, the photosynthetic protein machinery is challenging to modify and limited to biologically relevant pigments, which has hindered the exploration of nanoscale engineering for optimizing femtosecond to picosecond condensed-phase exciton dynamics.

In this issue of *Chem*, my colleagues and I develop a tunable DNA origami platform for controlling excitonic systems, including biomimetic light harvesting. We used time-resolved spectroscopy and computational methods to explore the photophysical parameters driving energy transport and exciton dynamics in these DNA origami circuits.[3] By incorporating multiple chromophores into DNA, we were able to generate delocalized excited states similar to those found in natural light-harvesting systems. The basis for fast and efficient light harvesting in condensed-phase systems lies in careful optimization of both the electronic coupling between chromophores and the system-bath coupling between chromophores and the environment. These parameters are dictated by chromophore placement and interaction with the surrounding protein pocket in natural systems. In our DNA systems, we achieved this required control over coupling by leveraging the predictable base pairing and structure formation of DNA to control both the interchromophore spacing and the surrounding DNA environment.

To quantify both the electronic coupling and the short-timescale system-bath coupling, we turned to ultrafast 2D electronic spectroscopy to map out dynamics with both temporal and spectral resolution. This method utilizes four coherent pulses in a non-collinear geometry (Figure 1A) to map out the correlation between excitation and emission frequencies (Figure 1B) and explore how these correlations change as a function of time after photoexcitation. This approach has been immensely useful in unraveling femtosecond dynamics in spectrally congested condensed-phase systems, and we have previously used the related technique, transient grating spectroscopy, to explore excited-state dynamics in non-DNA-bound chromophores.[4] We leveraged the correlative nature of this technique in two ways. First, we controlled the electronic coupling by varying the nucleotide spacing between neighboring chromophores. By correlating the excitation and emission frequency vibronic cross peaks in the 2D spectrum (Figure 1B) in conjunction with molecular dynamics simulations, we were able to tune the electronic coupling from the weak regime (tens of wavenumbers) to the strong regime (several hundred wavenumbers). In a second examination of the correlation spectrum, we used the 2D lineshape to extract the frequency-frequency correlation function, a

[1]Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, USA

*Correspondence: hart24@mit.edu

https://doi.org/10.1016/j.chempr.2021.02.008

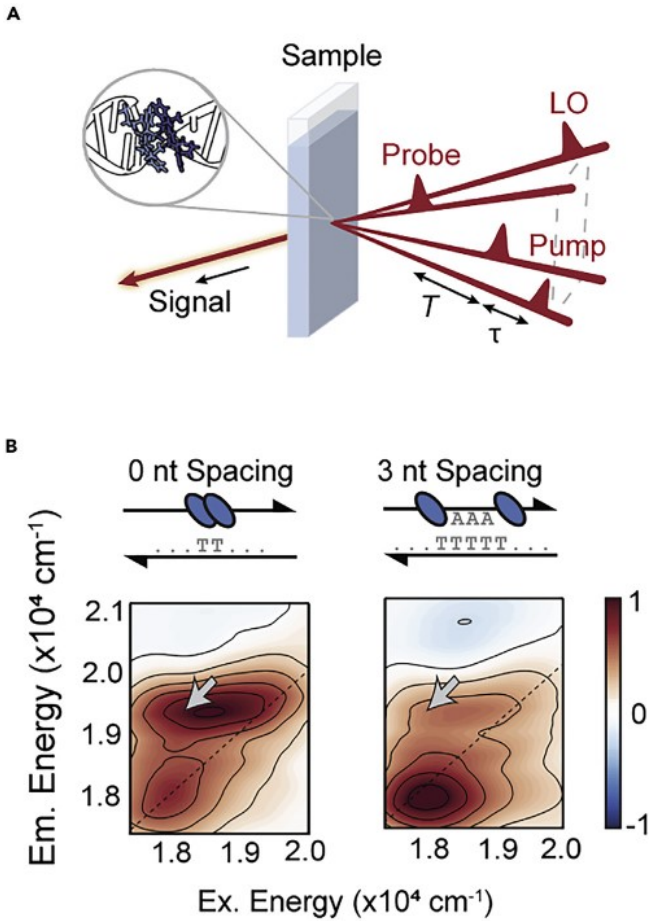

Figure 1. Using ultrafast spectroscopy to explore exciton dynamics

(A) Pulse sequence for 2D electronic spectroscopy used to investigate DNA exciton dynamics.
(B) Excitation-emission correlation spectra recovered from 2D electronic spectroscopy show upper-diagonal cross-peak signatures of electronic coupling.

spectral readout of the femtosecond-timescale system-bath interaction. We found evidence of sub-picosecond spectral diffusion and coupling to chromophore vibrational modes yet observed minimal differences in the short-time dynamics between the variation in DNA motifs on the nanometer length scale. This indicates that bath variations on longer timescales drive differences in energy-transfer dynamics in this system, suggesting that similar principles could be followed in other light-harvesting systems.

The systematic exploration of the parameters driving condensed-phase energy transfer in this work highlights the utility of DNA nanostructures in serving as artificial light harvesters. This approach also paves the way toward integration into other nanoscale devices for computation, imaging, and charge transport. Control over electronic coupling, system-bath coupling, and the extent of delocalization has particularly relevant implications for modular computing components, which can be both driven and measured by coherent spectroscopy methods. Advances in multiplexed imaging approaches could also be made with time-resolved spectroscopy studies of coupled DNA origami systems. In the future, design principles from these small-scale nanoengineered systems will hopefully inform the construction of more scalable excitonic systems such as metal-organic frameworks, semiconducting polymers, and other supramolecular constructs.

1. Blankenship, R.E. (2014). Molecular Mechanisms of Photosynthesis (John Wiley & Sons).

2. Schlau-Cohen, G.S., Akihito, I., and Fleming, G.R. (2011). Two-dimensional electronic spectroscopy and photosynthesis: Fundamentals and applications to photosynthetic light-harvesting. Chem. Phys. *386*, 1–22. https://doi.org/10.1016/j.chemphys.2011.04.025.

3. Hart, S.M., Chen, W.J., Banal, J.L., Bricker, W.P., Dodin, A., Markova, L., Vyborna, Y., Willard, A.P., Häner, R., Bathe, M., and Schlau-Cohen, G.S. (2021). Engineering couplings for exciton transport using synthetic DNA scaffolds. Chem *7*, this issue, 752–773.

4. Hart, S.M., Banal, J.L., Bathe, M., and Schlau-Cohen, G.S. (2020). Identification of nonradiative decay pathways in Cy3. J. Phys. Chem. Lett. *11*, 5000–5007. https://doi.org/10.1021/acs.jpclett.0c01201.