Studies of vibronically coupled molecular dimers in DNA by time-resolved two-dimensional fluorescence spectroscopy

Andrew H. Marcus,[1,*] Loni Kringle,[1] Mari Saif,[1] Nicolas Sawaya,[2] and Alán Aspuru-Guzik[2]

[1.] Department of Chemistry and Biochemistry, Oregon Center for Optical, Molecular and Quantum Science, Institute of Molecular Biology, University of Oregon, Eugene, OR 97403, USA

[2.] Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA, [*]ahmarcus@uoregon.edu

Two-dimensional fluorescence spectroscopy (2DFS) is used to study the local conformations and excited state dynamics of pairs of cyanine dyes, which are site-specifically incorporated into the sugar-phosphate backbones of DNA replication fork constructs. A vibronic coupling model describes time-resolved 2DFS, circular dichroism (CD), and linear dichroism (LD) of these systems.

The local conformations adopted by DNA are important to fundamental processes of gene regulation, including the functional assembly of protein-DNA complexes [1]. We present time-resolved two-dimensional fluorescence spectroscopic (2DFS) studies [2] of the local conformations adopted by vibronically coupled cyanine (Cy3) dyes, which are site-specifically positioned within the sugar-phosphate backbones of DNA replication fork constructs. As shown in Fig. 1, the Cy3 dyes replace bases on opposite strands of a DNA duplex. Recent 2D electronic coherence studies of covalently bound Cy3-Cy3 dimers have shown that vibronic coupling models can describe the delocalized excited states and dynamics of these systems [3]. In Cy3-Cy3 DNA constructs, dipolar coupling is sensitive to the placement of the chromophores relative to the DNA fork junction, and to temperature. We show that a vibronic coupling model can successfully account for time-resolved 2DFS, circular dichroism (CD), and absorption spectra of the coupled dimer, in addition to the linear dichroism (LD) spectrum of the Cy3 monomer in stretched polymer films.

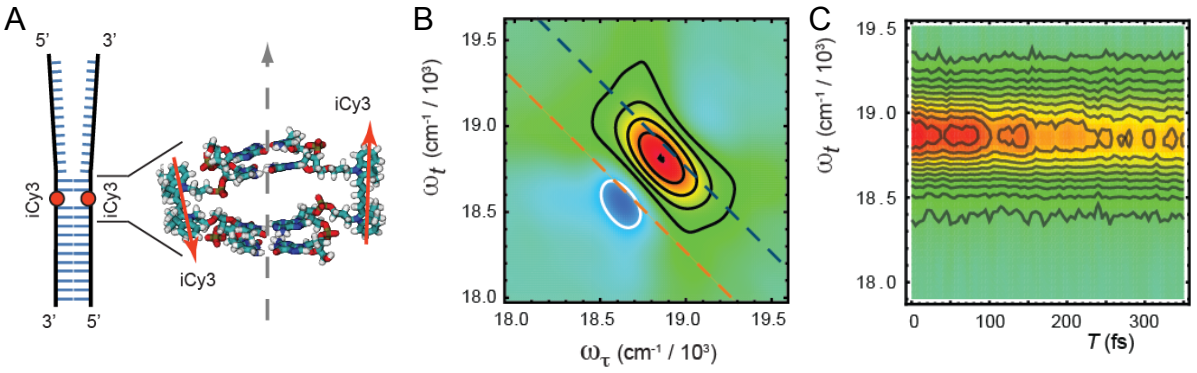

Figure 1. (A) An example of a DNA fork construct with two internally labeled Cy3 chromophores on opposite strands. A molecular model shows a possible structure in which the chromophores are rigidly positioned within the sugar-phosphate backbone. **(B)** Non-rephasing 2D fluorescence spectrum (with population time $T = 0$) of the construct shown in A. The laser spectrum was tuned to span the (0,0) and (0,1) vibronic feature of the Cy3 monomer. **(C)** Time-dependent anti-diagonal slice of the peak amplitude of the 2D spectrum shown in B. A prominent coherent beating occurs with period ~ 70 fs, and comparable dephasing time.

[1] von Hippel *et al.*, Biopolymers, **99**, 923 (2013).
[2] Perdomo-Ortiz *et al.*, J. Phys. Chem. B **116**, 10757 (2012).
[3] Halpin *et al.*, Nat. Chem. **6**, 196 (2014).