Supporting Information for:

Ground and Excited State Electronic Spectra of Perylenediimide Dimers with Flexible and Rigid Geometries in DNA Conjugates

Prakash P. Neelakandan, Tarek A. Zeidan, Martin McCullagh, George C. Schatz,
Josh Vura-Weis, Chul Hoon Kim, Michael R. Wasielewski and Frederick D. Lewis*

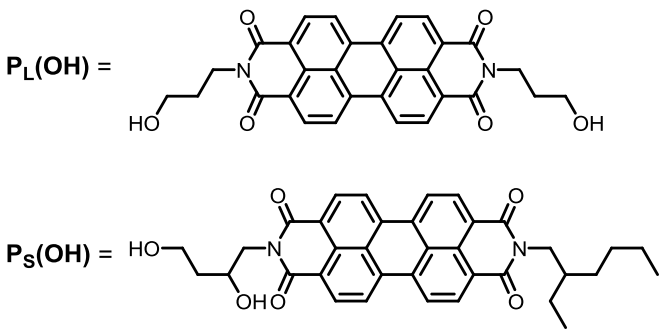

Chart S1

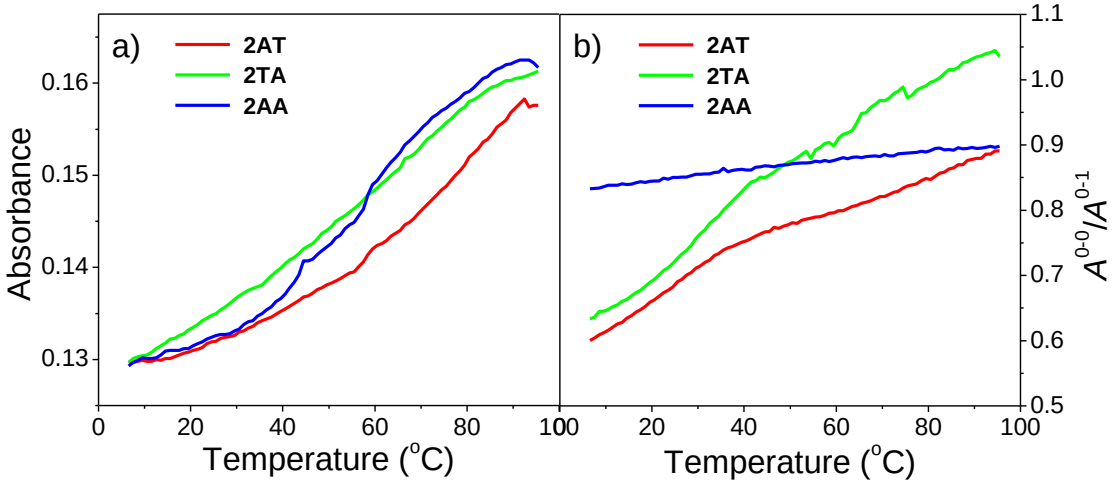

Fig. S1. (a) UV melting curves monitored at 260 nm and (b) the $A^{0\text{-}1}/A^{0\text{-}0}$ band intensity ratio for hairpins **2AT**, **2TA** and **2AA** in phosphate buffer.

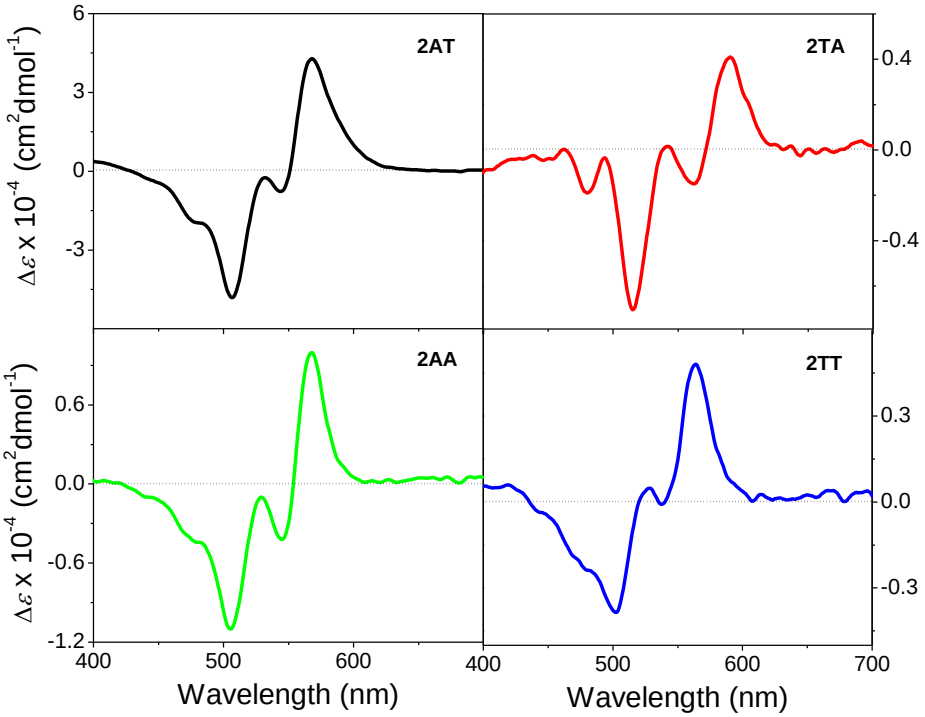

Fig. S2. Long wavelength region of the CD spectra of the hairpins **2AT**, **2TA**, **2AA** and **2TT** in phosphate buffer.

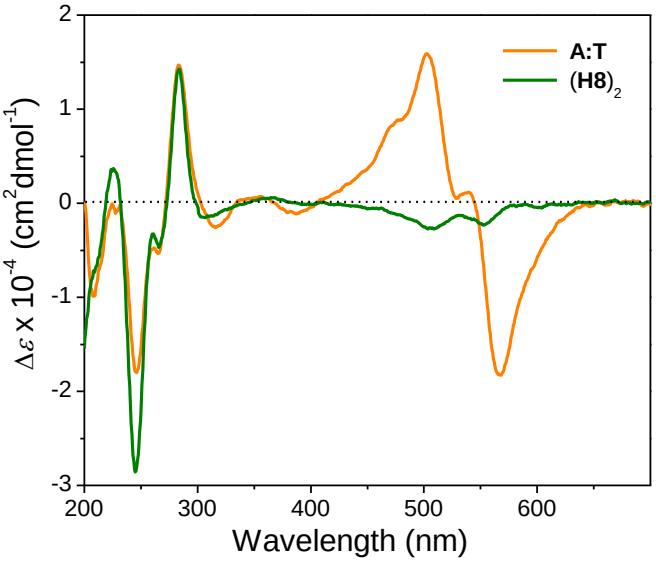

Fig. S3. Circular dichroism spectra of hairpin dimer $(\mathbf{H8})_2$[1] and duplex **A:T** in buffer.

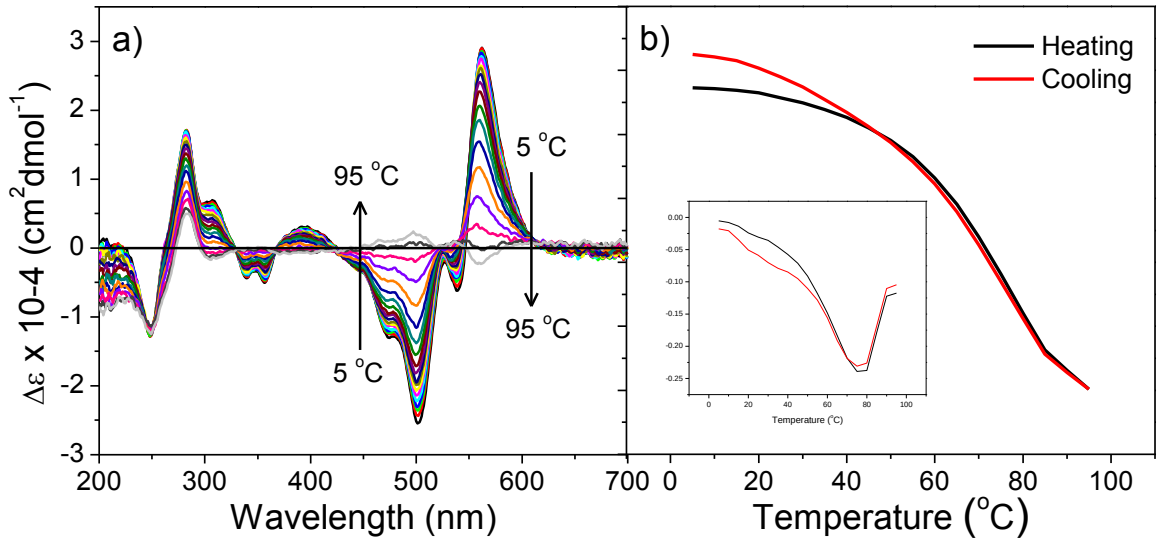

Fig. S4. (a) Temperature dependent CD spectra for **2AT** (ca. 1 μM hairpin in 10 mM phosphate buffer with 0.1 M NaCl). (b) Temperature dependence of the 560 nm band intensity. Inset shows derivative of 560 nm heating and cooling curves.

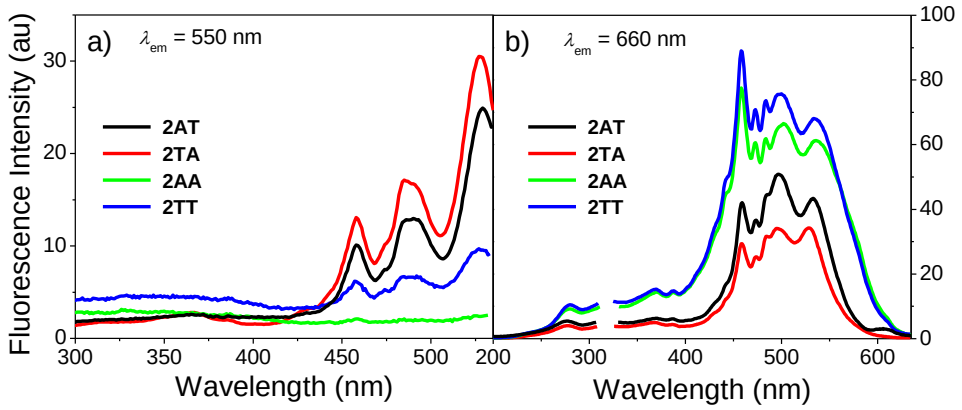

Fig. S5. Fluorescence excitation spectra of the hairpins **2AT**, **2TA**, **2AA** and **2TT** monitored at (a) 550 and (b) 660 nm in buffer. The spectra of **2AA** and **2TT** have been multiplied by a factor of 10 in (a) for clarity.

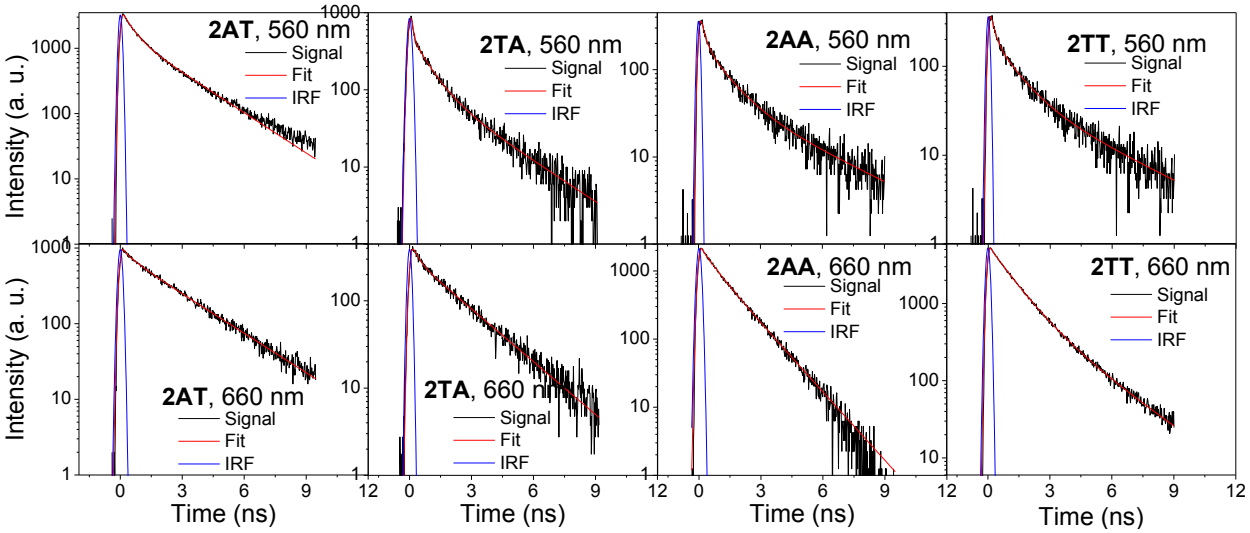

Fig. S6. Fluorescence decay profiles of various oligonucleotide conjugates at 560 (top) and 660 nm (bottom) in buffer.

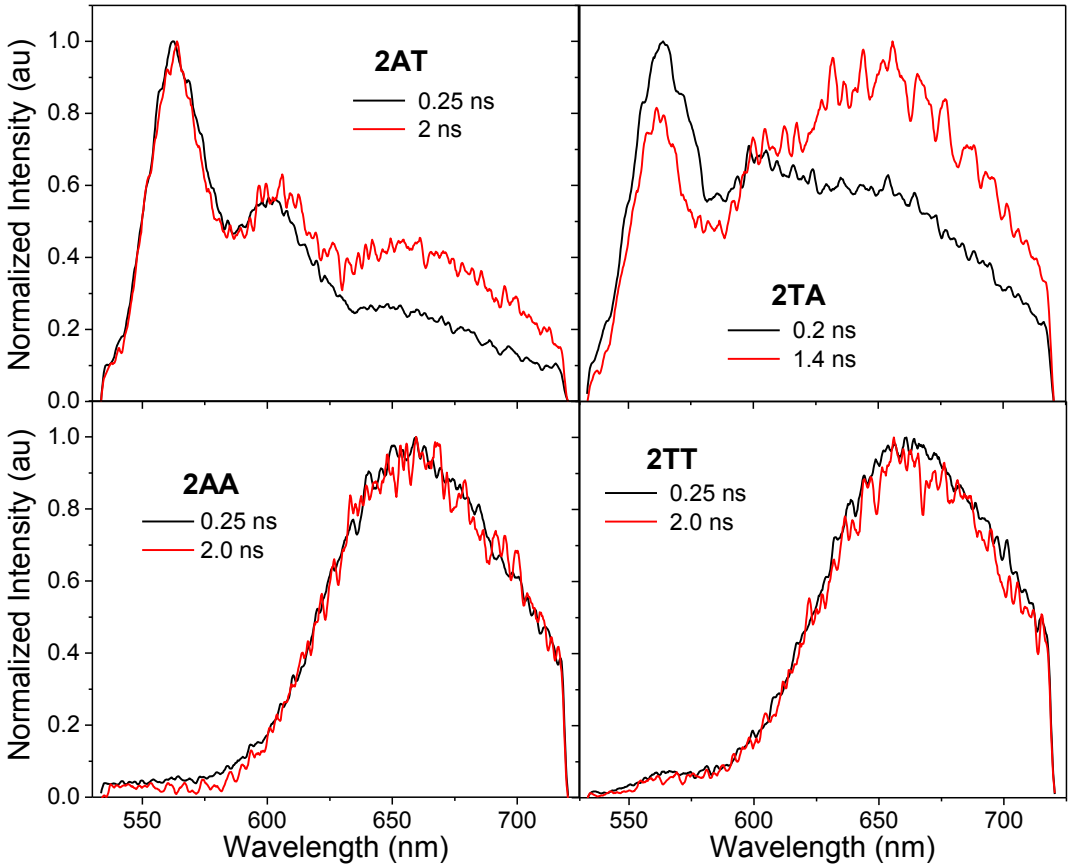

Fig. S7. Time resolved emission spectra of various oligonucleotides in buffer. Sample concentration and experimental conditions same as for fluorescence lifetime measurements.

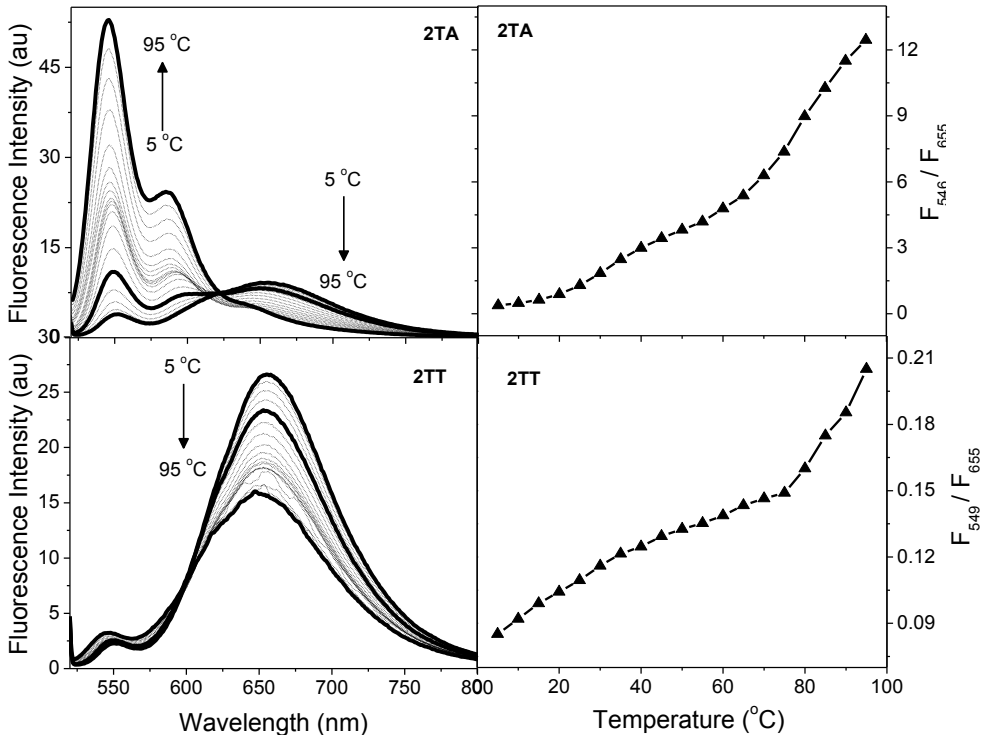

Fig. S8. (Left) Fluorescence spectra and (right) the ratio of monomer to excimer fluorescence intensities of **2TA** and **2TT** as a function of temperature in buffer. Bold traces in the middle indicate the fluorescence spectra at 25 °C. Excitation wavelength, 505 nm.

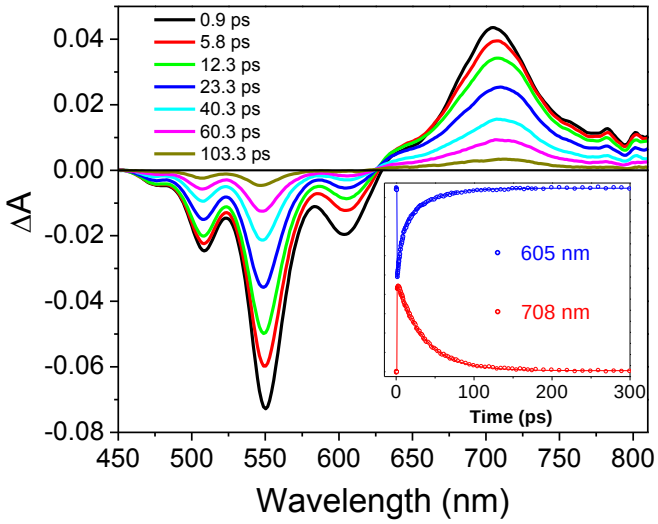

Fig. S9. Transient absorption spectra of hairpin **1A** in TE buffer (20 mM Tris, 2 mM EDTA), pH = 7.4, following excitation with 505 nm, 120 fs laser pulses. Inset: transient absorption kinetics at (◦◦◦◦) 605 nm and at (◦◦◦◦) 708 nm. Nonlinear least-squares fits to the data are also shown (data from Zeidan et al.).[2]

References

1. M. Hariharan, Y. Zheng, H. Long, T. A. Zeidan, G. C. Schatz, J. Vura-Weis, M. R. Wasielewski, X. B. Zuo, D. M. Tiede and F. D. Lewis, *J. Am. Chem. Soc.*, 2009, **131**, 5920-5929.
2. T. A. Zeidan, R. Carmieli, R. F. Kelley, T. M. Wilson, F. D. Lewis and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2008, **130**, 13945-13955.