Excited State Proton Transfer of Natural Flavonoids And Their Chromophores In Duplex And Tetraplex DNA

Bidisha Sengupta[*1], Samantha M. Reilly[2], Donald Davis Jr.[1], Kisa Harris[1], Randy M. Wadkins[2], Denise Ward[1], D'Asia Gholar[1], Cari Hampton[1]*

[1]*Department of Chemistry, Tougaloo College, Tougaloo, MS 39174*

[2]*Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677*

[*] Corresponding author:

Bidisha Sengupta, Department of Chemistry, Tougaloo College, Tougaloo, MS 39174, U.S.A.

email: bsengupta@tougaloo.edu; bsgupta.tougaloo@gmail.com (phone: +1-601-977-7779, FAX: +1-601-977-7898)

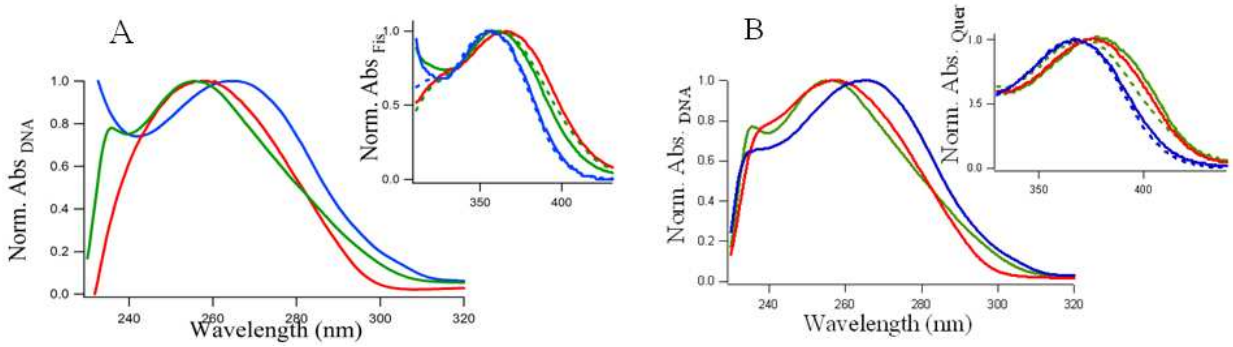

Figure S1. Normalized absorbance of fisetin (A) and quercetin (B) bound single stranded 5'-d$(C_3T_2A)_3C_3$ (blue) in pH 6, 5'-d$(T_2AG_3)_4$ (green) in pH 7 and double stranded DNA (red) in pH 7 buffers made up of 10 mM citrate. The inset shows the absorbance of fisetin (A) and quercetin (B) conjugated in the above mentioned DNAs. The blue and green dashed lines display the absorbance of fisetin (A) and quercetin (B) in pH 6 and 7 buffers respectively. The λ_{abs}^{max} of fisetin is ~ 360, 361 and 366 nm and quercetin is ~ 368, 380 and 376 nm in 5'-d$(C_3T_2A)_3C_3$, 5'-d$(T_2AG_3)_4$, and the duplex DNA respectively.

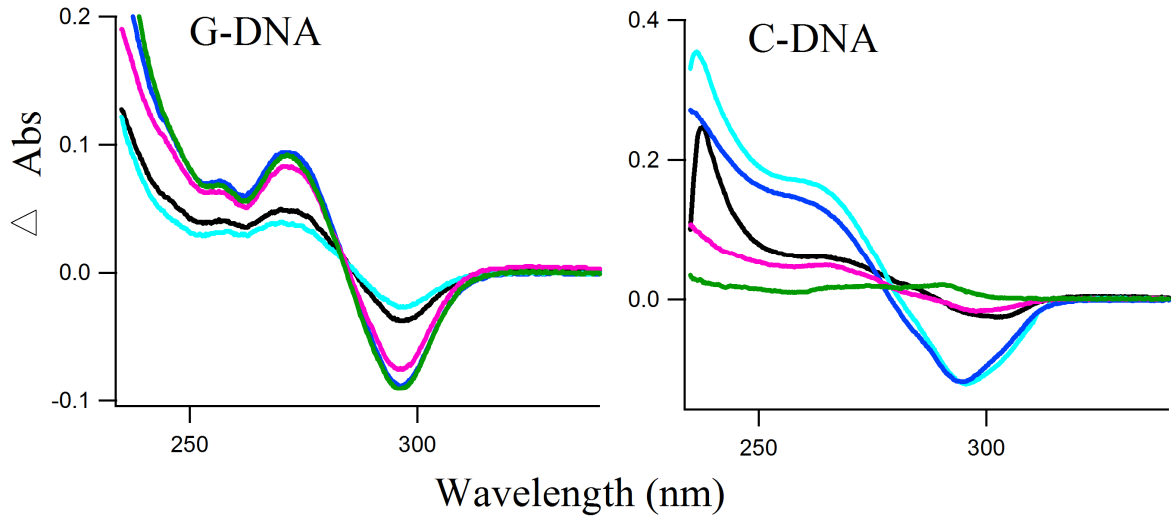

Figure S2. Differential absorption spectra of $d(T_2AG_3)_4$ (left) and $d(C_3T_2A)_3C_3$ (right) in different pHs. Lines black, cyan, blue, purple, green represent pH 5, 5.5, 6, 6.5 and 7 respectively.

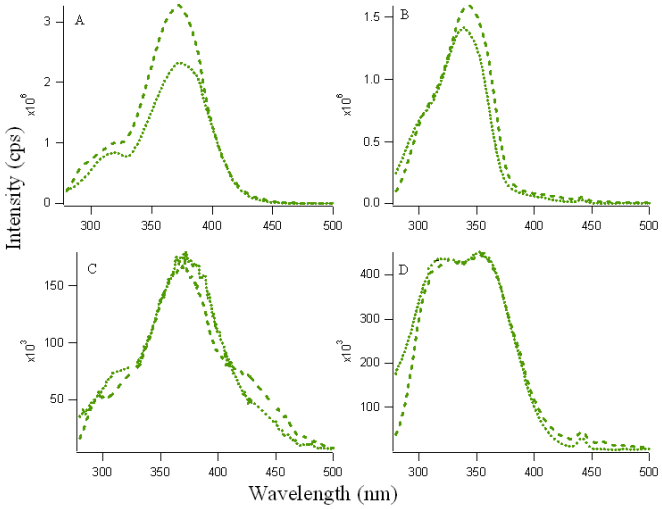

Figure S3. Fluorescence excitation (at λ_{em}=530 nm) for fisetin (A), 3-hydroxyflavone (B), quercetin (C) and 7-hydroxyflavone (7HF) in 0 (……) and 20 μM G_4 DNA (- - - - -) at 25^0 C, [Fisetin] = 1.0 x 10^{-5} M.

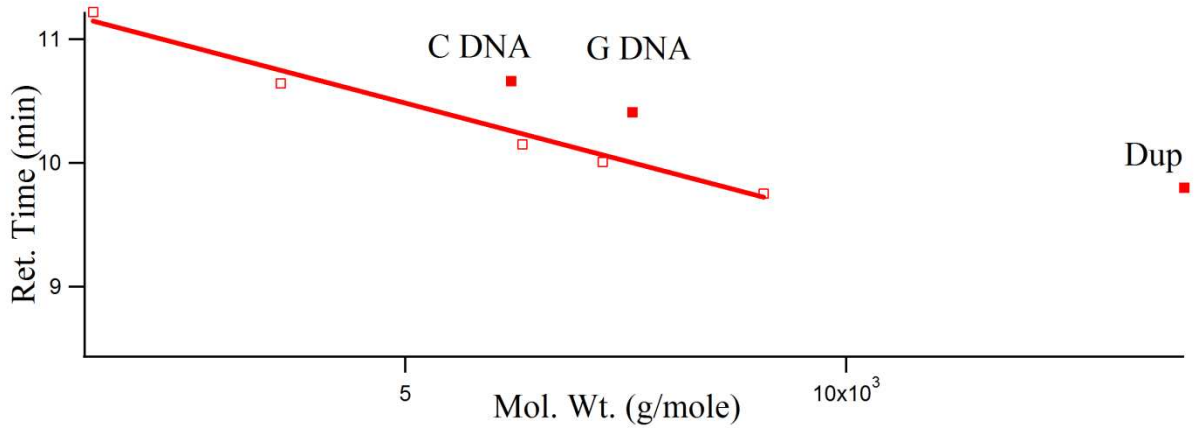

Figure S4. The calibration curve of the size standards (T_5, T_{12}, T_{21}, T_{24}, T_{30}) to relate the retention times on the column to the molecular masses. The mobile phase is 10 mM citrate buffer, at pH 7 with 100 mM $NaClO_4$. The retention times of $d(C_3T_2A)_3C_3$ (C DNA), $d(T_2AG_3)_4$ (G DNA) and duplex (Dup) are indicated in the plot with the red solid squares, which is out of the linear fit in the calibration plot, displaying and indicating the folded nature of the singles stranded C, G rich oligonucleotides along with their duplex form.

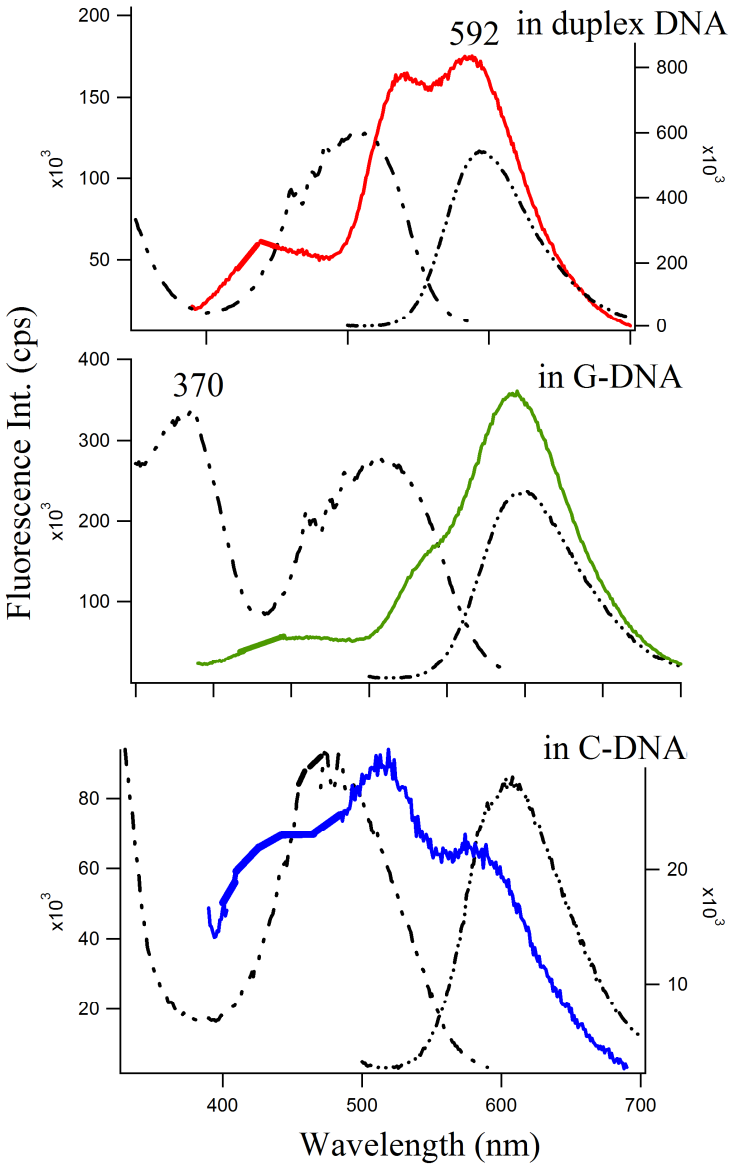

Figure S5. Fluorescence emission (solid line) of 5 µM quercetin (λ_{ex} = 370 nm) in 10 µM DNA (C_4 (blue), G_4 (green) and duplex (red)) in presence of EtBr. The black profiles correspond to emission of 5 µM EtBr (λ_{ex} = 480 nm) in 10 µM DNA (-..- in the presence of 5 µM quercetin). The figure also shows the excitation spectra of EtBr (λ_{em} = 610 nm) in DNA with quercetin (black —. .—).