Direct Chemical Evidence for Charge Transfer between Photoexcited 2-Aminopurine and Guanine in Duplex DNA

Melanie A. O'Neill, Chikara Dohno and Jacqueline K. Barton

Division of Chemistry and Chemical Engineering
California Institute of Technology,
Pasadena, California 91125

Supporting Information

Figure S-1. Reverse phase HPLC (C18, 2-14 % acetonitrile in 50 mM ammonium acetate over 30 minutes) traces profiling the decomposition of ^{CP}G as a function of irradiation time (325 nm, ~ 3 mW) for 5 μM ApAAC^{CP}G duplexes in 100 mM sodium phosphate pH 7. Expanded region shows formation of ^{HP}G as a function of increasing irradiation time. These traces are representative of those observed for all Ap/^{CP}G duplexes with the exception of ApC^{CP}G and ApA^{CP}G for which no photodecomposition was observed.

Figure S-2. Fluorescence emission spectra (λ_{ex} = 325 nm) of 5 μM Ap/^{CP}G duplexes in 100 mM sodium phosphate pH 7. All duplexes are dramatically less emissive (< 5 %) than free Ap under the same conditions. The following trends in the relative quenching of Ap within the DNA duplexes are noted: ApAG > ApA^{CP}G; ApAAA^{CP}G > ApA^{CP}G; ApAAAAC^{CP}G-A-A mismatch > ApAAAAC^{CP}G > ApAAC^{CP}G. These are consistent with the influence of donor (G, or ^{CP}G) distance and oxidation potential (^{CP}G < G), neighboring bases (purines versus pyrimidines) and nearby mismatches on Ap* emission intensity.

Figure S-3. Normalized fluorescence excitation spectra (λ_{em} = 370 nm) of Ap and Ap/^{CP}G duplexes. Samples are 5 μM in 100 mM sodium phosphate pH 7. The long wavelength band, due to direct excitation of Ap is redshifted in DNA. The magnitude of this shift reflects the reduction in solvent exposure of Ap within the duplex. The short wavelength band is due to energy transfer from the natural DNA bases; stronger stacking interactions facilitate more efficient energy transfer. Both the relative redshift and the relative intensity of the energy transfer band increase in the following order: Ap < ApC^{CP}G < ApA^{CP}G = ApAG. This indicates that Ap does not sense the substitution of ^{CP}G for G, and that as with G, stacking interactions of Ap in ^{CP}G duplexes are stronger with A than with C.

Table S-1. Melting temperatures (T_m) of Ap/^{CP}G duplexes (3 μM in 100 mM sodium phosphate pH 7) determined by monitoring the change in absorption at 260 nm as a function of temperature (0.5 ^{o}C/minute). The T_m corresponds to the maximum ΔA/ΔT. In duplex 7, the A-A mismatch is at the third A from the 5'-end. Note that duplexes 4-7 have a slightly higher GC content (exchange of one GC for AT pair) than duplexes 1-3 leading to a small increase in duplex stabilization.

Number	Duplex	T_m (^{o}C)
1	ApAG	65
2	ApA^{CP}G	64
3	ApAAA^{CP}G	65
4	ApC^{CP}G	68
5	ApAAC^{CP}G	68
6	ApAAAAC^{CP}G	68
7	ApAAAAC^{CP}G A-A mismatch	65

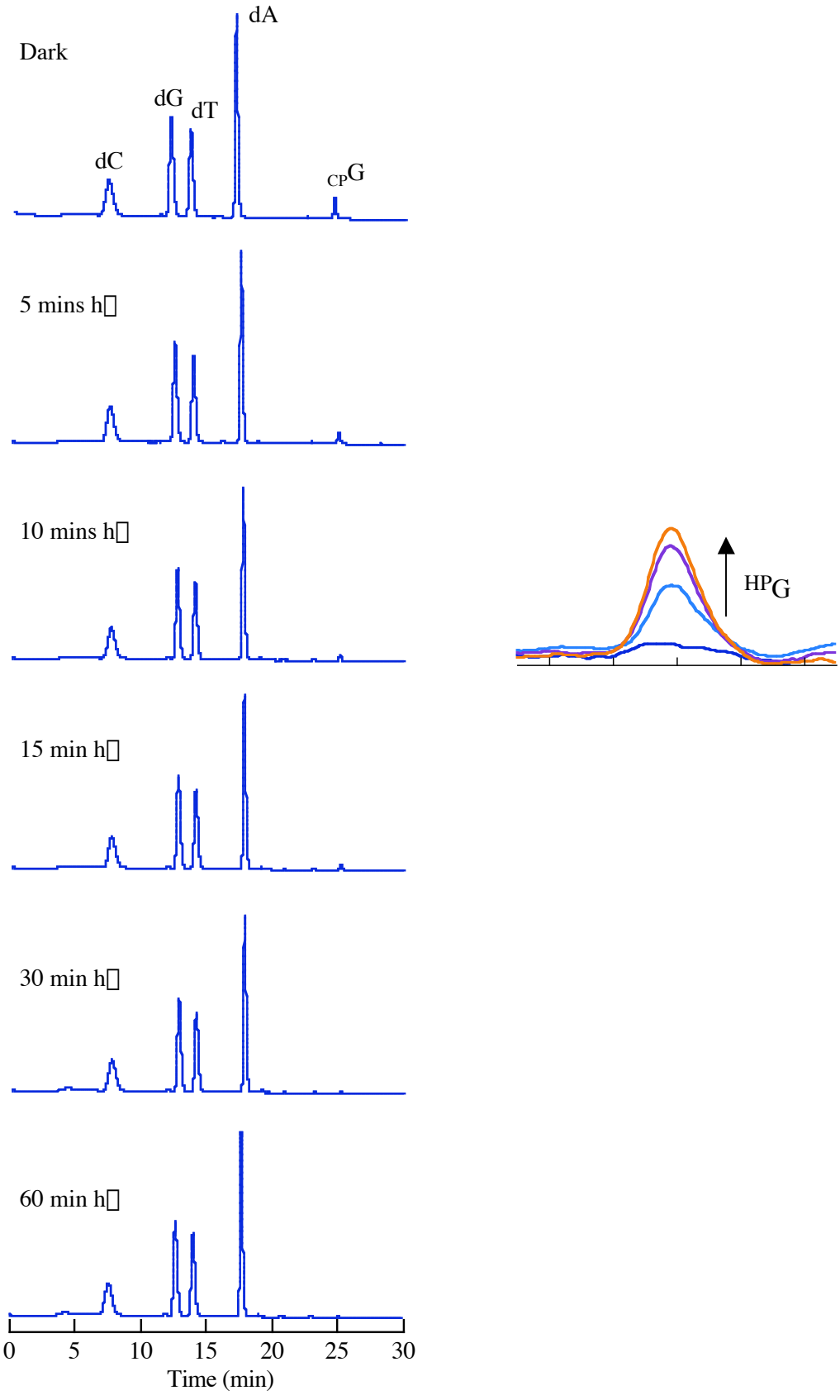
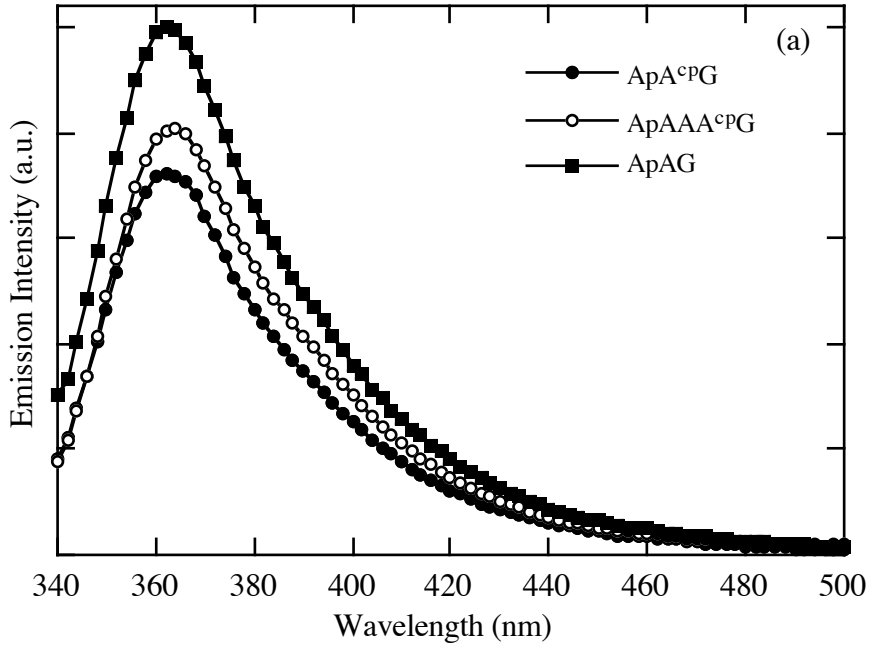

Dark
dA
dG
dT
dC
CPG
5 mins h
10 mins h
15 min h
30 min h
60 min h
HPG
0
5
10
15
20
25
30
Time (min)

Figure S-1


(a)
ApA^cpG
ApAAA^cpG
ApAG
Emission Intensity (a.u.)
340
360
380
400
420
440
460
480
500
Wavelength (nm)

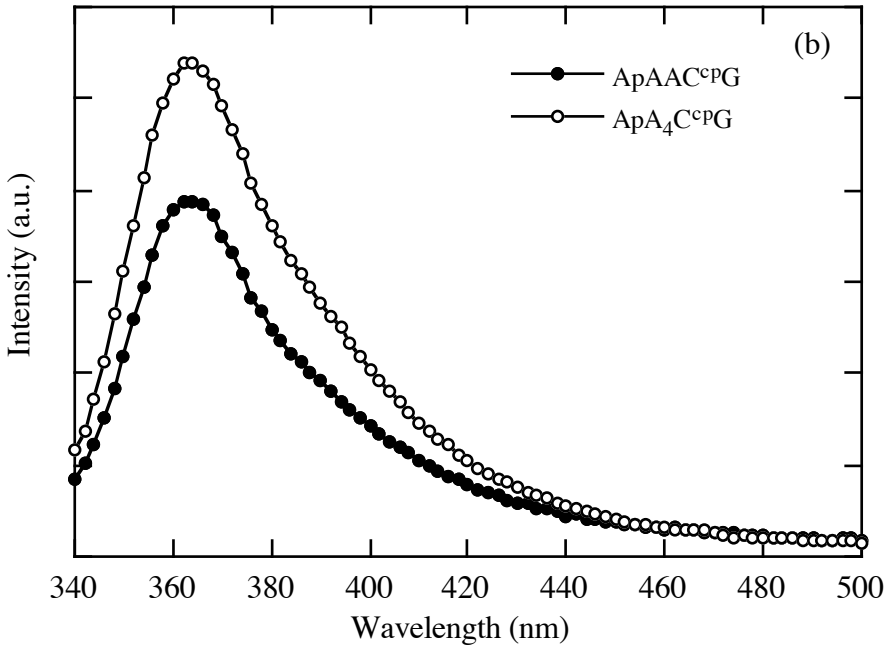

(b)
ApAAC^cpG
ApA4C^cpG
Intensity (a.u.)
340
360
380
400
420
440
460
480
500
Wavelength (nm)

Figure S-2

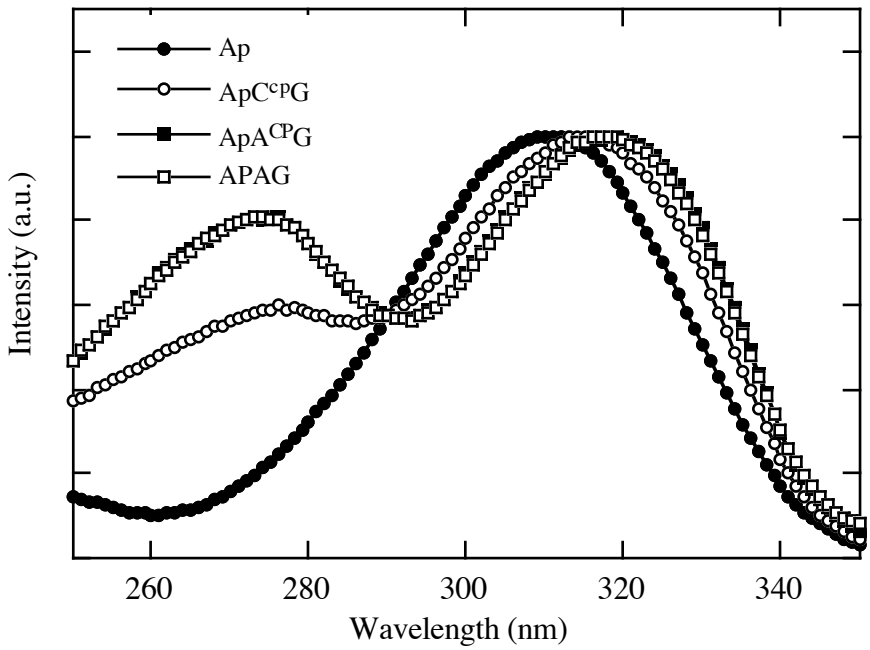

Ap
ApC^cpG
ApA^CpG
APAG
Intensity (a.u.)
260
280
300
320
340
Wavelength (nm)

Figure S-3