Supplementary Information

Single Step Charge Transport Through DNA over Long Distances

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Table S1: DNA Assemblies for Oxidative Decomposition Experiments

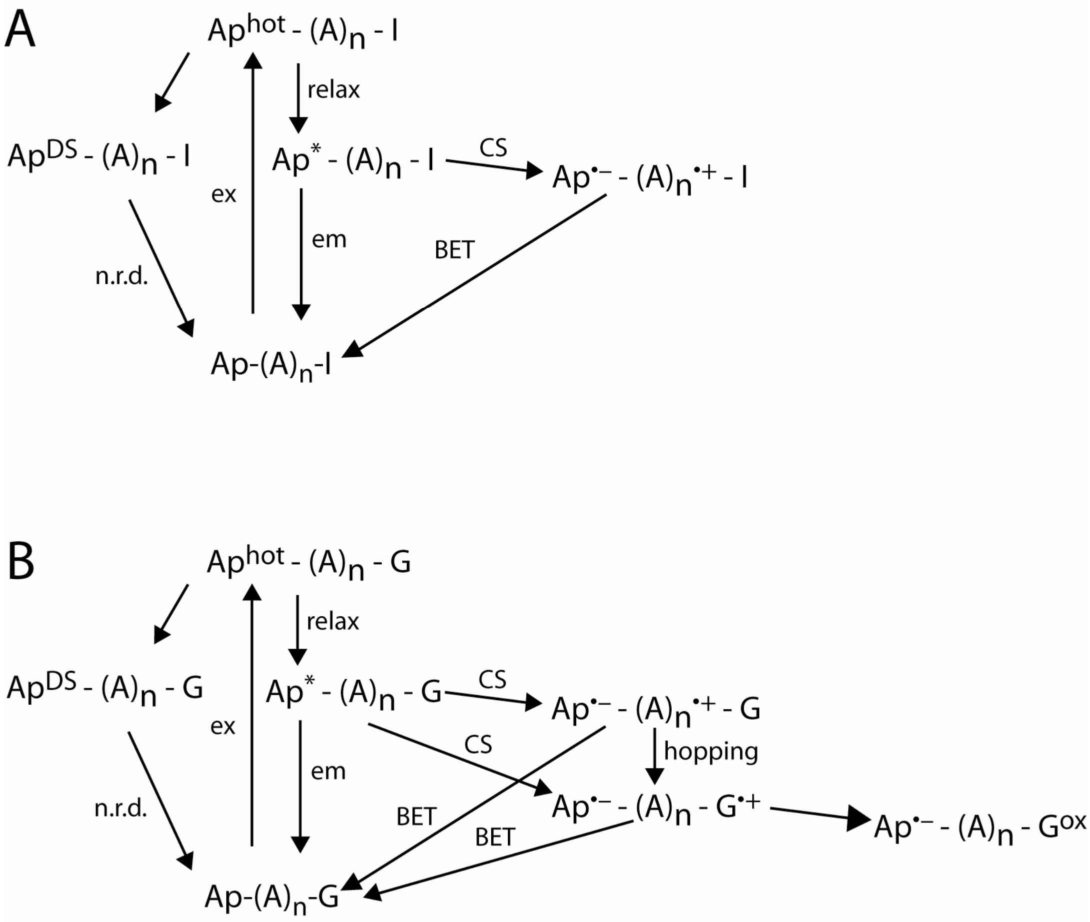
Ap-A_0-^{CP}G	5'-GATTATAGACATATT**IAp-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT - C**CATAATTCATGTAATG-5’
Ap-A_1-^{CP}G	5'-GATTATAGACATATT**IAp-A-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -T- C**CATAATTCATGTAATG-5’
Ap-A_2-^{CP}G	5'-GATTATAGACATATT**IAp-AA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT- C**CATAATTCATGTAATG-5’
Ap-A_3-^{CP}G	5'-GATTATAGACATATT**IAp-AAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTT - C**CATAATTCATGTAATG-5’
Ap-A_4-^{CP}G	5'-GATTATAGACATATT**IAp-AAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTT- C**CATAATTCATGTAATG-5’
Ap-A_5-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTT - C**CATAATTCATGTAATG-5’
Ap-A_6-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTTT - C**CATAATTCATGTAATG-5’
Ap-A_7-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTTTT - C**CATAATTCATGTAATG-5’
Ap-A_8-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT - TTTTTTTT - C**CATAATTCATGTAATG-5’
Ap-A_9-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAAAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTTTTTT - C**CATAATTCATGTAATG-5’
Ap-A_{11}-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAAAAAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTTTTTTTT - C**CATAATTCATGTAATG-5’
Ap-A_{12}-^{CP}G	5'-GATTATAGACATATT**IAp-AAAAAAAAAAAA-^{CP}GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTTTTTTTTT - C**CATAATTCATGTAATG-5’
Ap-A_3-^{CP}A-A_4-I	5'-GATTATAGACATATT**IAp-AAA^{CP}AAAAA-I**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTT TTTT -C**ATAATTCATGTAATG-5’
Ap-A_6-^{CP}A-I	5'-GATTATAGACATATT**IAp-AAAAAA^{CP}A-I**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTTTT T-C**ATAATTCATGTAATG-5’
LC-A_6-^{CP}A-I	5'-GATTATAGACATATT**I A-AAAAAA^{CP}A-I**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT-TTTTTT T-C**ATAATTCATGTAATG-5’
Ap-A_2-^{CP}A-A_2-I	5'-GATTATAGACATATT**IAp-AA^{CP}AAA-II**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT TTT-CC**ATAATTCATGTAATG-5’

Ap-A$_2$-^{CP}A-A$_2$-G	5'-GATTATAGACATATT**IAp-AA**^{CP}**AAA-GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT TTT-CC**ATAATTCATGTAATG-5’
Ap-A$_2$-^{CP}A-A$_2$-^{CP}G	5'-GATTATAGACATATT**IAp-AA**^{CP}**AAA-**^{CP}**GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT TTT - CC**ATAATTCATGTAATG-5’
Ap-A-^{CP}A-A$_3$-I	5'-GATTATAGACATATT**IAp-A**^{CP}**AAAA- II**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -T TTTT-CC**ATAATTCATGTAATG-5’
Ap-A$_3$-^{CP}A-A-I	5'-GATTATAGACATATT**IAp-AAA**^{CP}**AA-II**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTT TT-CC**ATAATTCATGTAATG-5’
Ap-A$_4$-^{CP}A-I	5'-GATTATAGACATATT**IAp-AAAA**^{CP}**A - I I**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TTTT T-CC**ATAATTCATGTAATG-5’
Ap-A$_2$-^{CP}A-A$_3$-I	5'-GATTATAGACATATT**IAp-AA**^{CP}**AAAA-I I**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT TTTT-CC**ATAATTCATGTAATG-5’
Ap-A$_2$-^{CP}A-A$_3$-G	5'-GATTATAGACATATT**IAp-AA**^{CP}**AAAA-GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT TTTT-CC**ATAATTCATGTAATG-5’
Ap-A$_2$-^{CP}A-A$_3$-^{CP}G	5'-GATTATAGACATATT**IAp-AA**^{CP}**AAAA-**^{CP}**GI**TATTAAGTACATTAC-3’ 3’-CTAATATCTGTATAA**CT -TT TTTT- C C**ATAATTCATGTAATG-5’

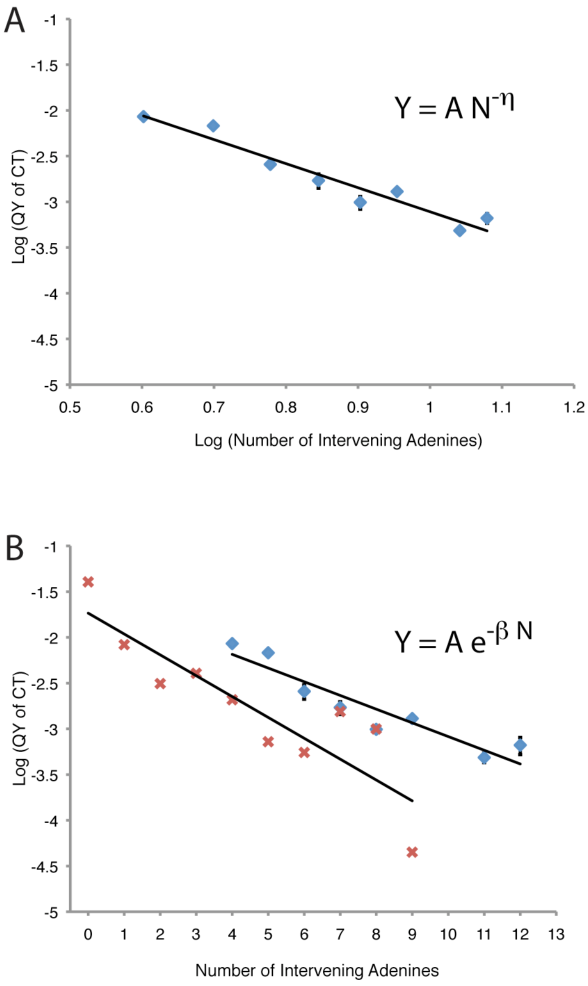
Table S2. Quantum yields of decomposition for CP-modified bases

Sequence	Quantum Yield of Decomposition
Ap-A_0-^{CP}G	0.00008 ± 0.00010[a]
Ap-A_1-^{CP}G	0.00002 ± 0.00008
Ap-A_2-^{CP}G	0.00029 ± 0.00016
Ap-A_3-^{CP}G	0.00344 ± 0.00009
Ap-A_4-^{CP}G	0.0086 ± 0.0002
Ap-A_5-^{CP}G	0.0068 ± 0.0005
Ap-A_6-^{CP}G	0.0026 ± 0.0005
Ap-A_7-^{CP}G	0.0017 ± 0.0003
Ap-A_8-^{CP}G	0.00099 ± 0.00003
Ap-A_9-^{CP}G	0.0013 ± 0.0001
Ap-A_{11}-^{CP}G	0.00049 ± 0.00006
Ap-A_{12}-^{CP}G	0.0007 ± 0.0001
Ap-A_3-^{CP}A-A_4-I	0.0096
Ap-A_6-^{CP}A-I	0.00096
LC-A_6-^{CP}A-I	0.000066
Ap-A_2-^{CP}A-A_2-I	0.0019 ± 0.0002
Ap-A_2-^{CP}A-A_2-G	0.0020 ± 0.0002
Ap-A_2-^{CP}A-A_2-^{CP}G	0.0017 ± 0.0002 (^{CP}A)
Ap-A_2-^{CP}A-A_2-^{CP}G	0.0011 ± 0.0003 (^{CP}G)
Ap-A-^{CP}A-A_3-I	0 ± 0.0002
Ap-A_3-^{CP}A-A-I	0.0061 ± 0.0002
Ap-A_4-^{CP}A-I	0.0021 ± 0.0002
Ap-A_2-^{CP}A-A_3-I	0.0022 ± 0.0002
Ap-A_2-^{CP}A-A_3-G	0.0020 ± 0.0001
Ap-A_2-^{CP}A-A_3-^{CP}G	0.0023 ± 0.0002 (^{CP}A)
Ap-A_2-^{CP}A-A_3-^{CP}G	0.0004 ± 0.0003 (^{CP}G)

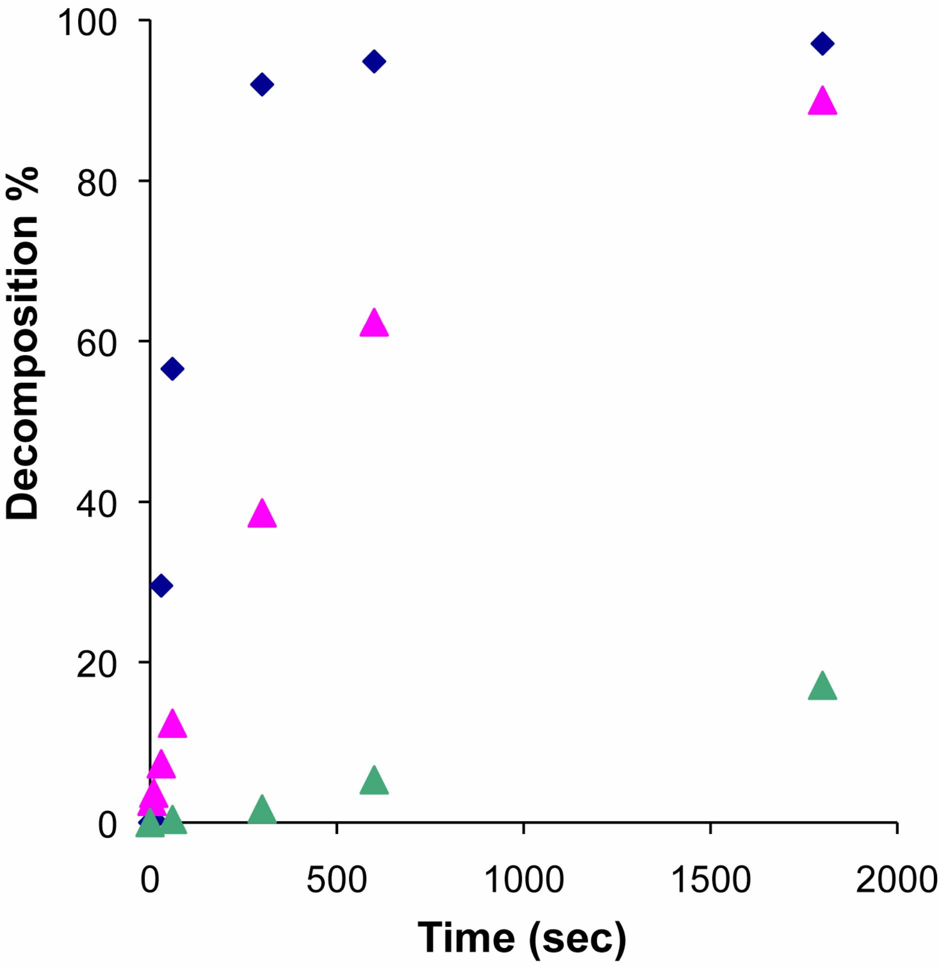
a. Errors are reported as 90% s.e.m.



Supplementary Figure 1



Supplementary Figure 2



Supplementary Figure 3

Figure S1. Excited state dynamics of aminopurine in DNA. All duplexes are initially excited (ex) to a hot state (Ap^{hot}), which can either decay through a non-radiative pathway (n.r.d.) through a dark state (DS), or relax to the persistent excited state (Ap^{*}). Assemblies that are not in a CT-active state with respect to guanine, or that contain inosine instead of guanine (**A**), can undergo either emission (em) or charge separation (CS) to generate the adenine cation radical, which regenerates the ground state upon back electron transfer (BET). If a guanine is present (**B**), the hole on adenine can hop to guanine. Guanine cation radical then decays by either ring-opening (in the ^{CP}G constructs) or BET. Relative heights are arbitrary.

Figure S2. Fits of distance-dependent CT yields for the Ap-A_n-^{CP}G series on a $\log_{10}$ (**A**) and semi$\log_{10}$ (**B**) scale. Conditions are as in Fig 2. For the total CT yield (blue diamonds), the data is comparably fit by geometric and exponential decay with distance. The decay constant from fitting to geometric decay, η, is 2.6. The decay constant from fitting to exponential decay, β, is 0.3 per base (0.1 $Å^{-1}$). The single-step CT yields (red x's) do not fit well to an exponential distance dependence, due to the periodicity.

Figure S3. Time courses of ^{CP}A decomposition by irradiation of Ap-A_3-^{CP}A-A_4-I (blue diamonds), Ap-A_6-^{CP}A-I (purple triangles), and the light control LC-A_6-^{CP}A-I (green triangles). The decomposition in each case follows first order kinetics. 10 μM duplexes were irradiated at 325 nm. Conditions are as provided in Methods.