Supplemental Information

for

UVA-visible photo-excitation of guanine radical cations produces sugar radicals in DNA and model structures

By

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Supplementary Material:

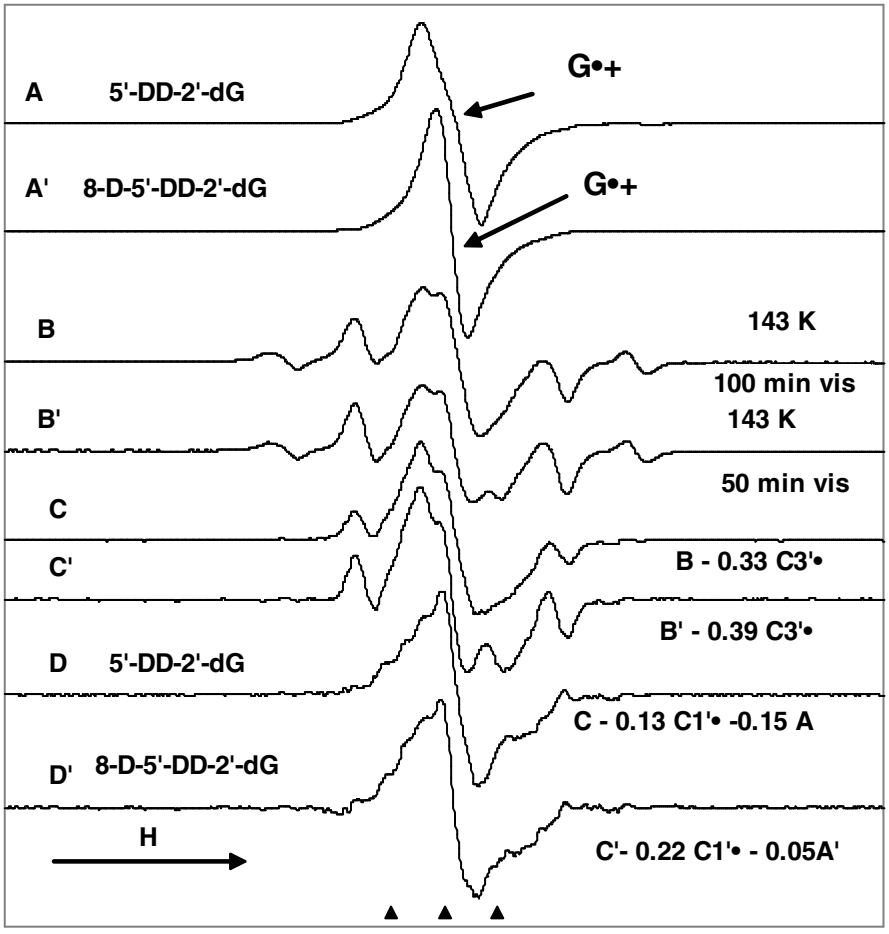

Figure S1. (A) and (A') represent the spectrum of $G^{\bullet+}$ formed in 5'-DD-2dG and 8-D-5'-DD-2'-dG respectively before illumination at 77 K in the presence of 5 mg $K_2S_2O_8$ in D_2O in 7 *M* LiCl glass which was γ-irradiated at 77K for 105 min followed by annealing at 150 K. (B) and (B') After visible illumination at 143 K, showing a nearly complete conversion to sugar radicals. (C) and (C') show the subtraction of C3'• (benchmark) in Figure 1C from B and B' respectively. (D) and (D') show that the 5'-DD-2dG and 8-D-5'-DD-2'-dG produce almost identical spectra after the requisite amount of subtraction of C1'• (benchmark) in Figure 1A and $G^{\bullet+}$. All ESR spectra are recorded at 77 K. The sample in A and A' has a red-violet color; those in B and B' were colorless.

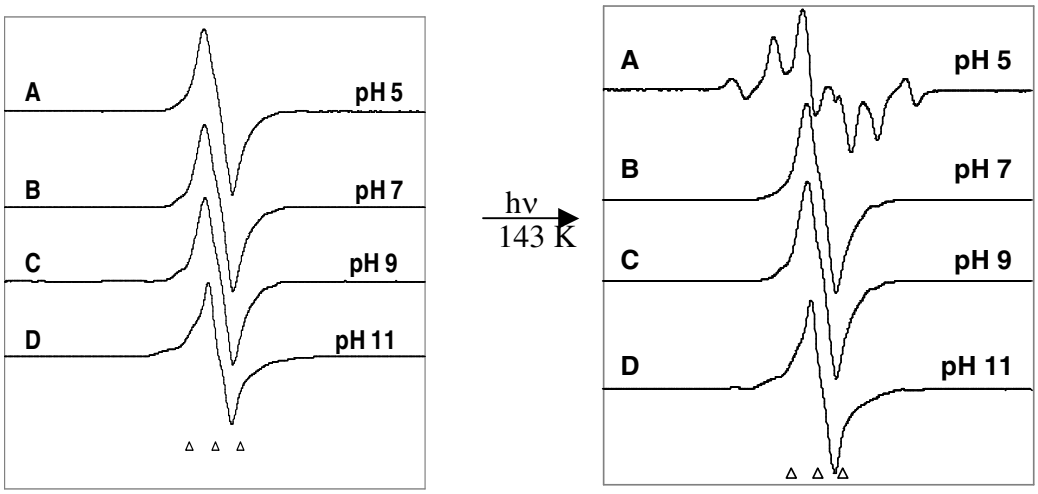

Figure S2. 2'-dG (3 mg) in the presence of 5 mg $K_2S_2O_8$ in D_2O in 7 *M* LiCl glass which was γ-irradiated at 77K for 105 min followed by annealing at 150K to produce $G^{\bullet+}$. The pH was adjusted by adding appropriate amounts of 1 *M* NaOH in D_2O.

The left hand spectra show the spectra from $G^{\bullet+}$ after irradiation and annealing. The right hand spectra show the same samples after illumination with visible light for 100 minutes (for spectrum A) with no filter present and this spectrum is same as that of Figure 5B. Substantial changes were noted even after 15 min of irradiation. For spectra B, C and D, all samples were illuminated for 30 min and as no significant changes were found, thus these spectra were taken only after 30 min of illumination. All spectra are recorded at 77 K.

Table S1

TD-DFT 6-311++G(d,p) Calculation for 2'deoxyguanosine
(Structure Optimized at DFT B3LYP 6-31G(d))

Method: TD-DFT
Basis Set: 6-311++G(d,p)
Functionals: B3LYP
Transitions: 16
Total Energy: -963.518542789 Hartrees

Excited State 1	**Energy (eV)**	**Wavelength (nm)**	**Oscillator Strength**
	1.4548	852.22	f=0.0009
68B->70B 0.817 (1 particle RhoCI Excited state density for |0.2| and above only)			
69B->70B -0.557			
Excited State 2	1.6482	752.22	f=0.0004
66B->70B -0.393			
68B->70B 0.506			
69B->70B 0.758			
Excited State 3	1.7449	710.54	f=0.0002
66B->70B 0.899			
68B->70B 0.212			
69B->70B 0.329			
Excited State 4	1.9371	640.04	f=0.0000
65B->70B 0.229			
67B->70B 0.940			
Excited State 5	1.9371	640.04	f=0.0000
64B->70B -0.618			
65B->70B 0.721			
67B->70B -0.295			
Excited State 6	2.5328	489.51	f=0.0067
62B->70B -0.361			
63B->70B 0.749			
64B->70B -0.384			
65B->70B -0.311			
Excited State 7	2.7877	444.76	f=0.0126
62B->70B 0.883			
63B->70B 0.402			
Excited State 8	2.9823	415.73	f=0.0001

62B->70B -0.208
63B->70B 0.450
64B->70B 0.646
65B->70B 0.558

Excited State 9 3.3623 368.75 f=0.0340
58B->70B 0.593
59B->70B 0.484
60B->70B 0.207
61B->70B -0.552

Excited State 10 3.4021 364.44 f=0.0506
70B->71B -0.227
58B->70B -0.515
59B->70B 0.522
60B->70B 0.198

Excited State 11 3.6703 337.80 f=0.0009
58B->70B 0.420
59B->70B 0.401
60B->70B -0.257
61B->70B 0.744

Excited State 12 3.7085 334.32 f=0.0014
58B->70B 0.407
59B->70B -0.460
60B->70B 0.724
61B->70B 0.285

Excited State 13 4.3669 283.92 f=0.1249
70B->71B -0.623
70B->72B 0.655
52B->70B -0.217

Excited State 14 4.4047 281.48 f=0.1282
70B->71B 0.650
70B->72B 0.669

Excited State 15 4.6126 268.79 f=0.0018
57B->70B 0.987

Excited State 16 4.8881 253.65 f=0.0012
68B->71B -0.306
69B->71B 0.206
56B->70B 0.850