Supporting Information

for

Photo-excitation of adenine cation radical [A•$^{+}$] in the near UV-vis region produces sugar radicals in Adenosine and in its nucleotides

By

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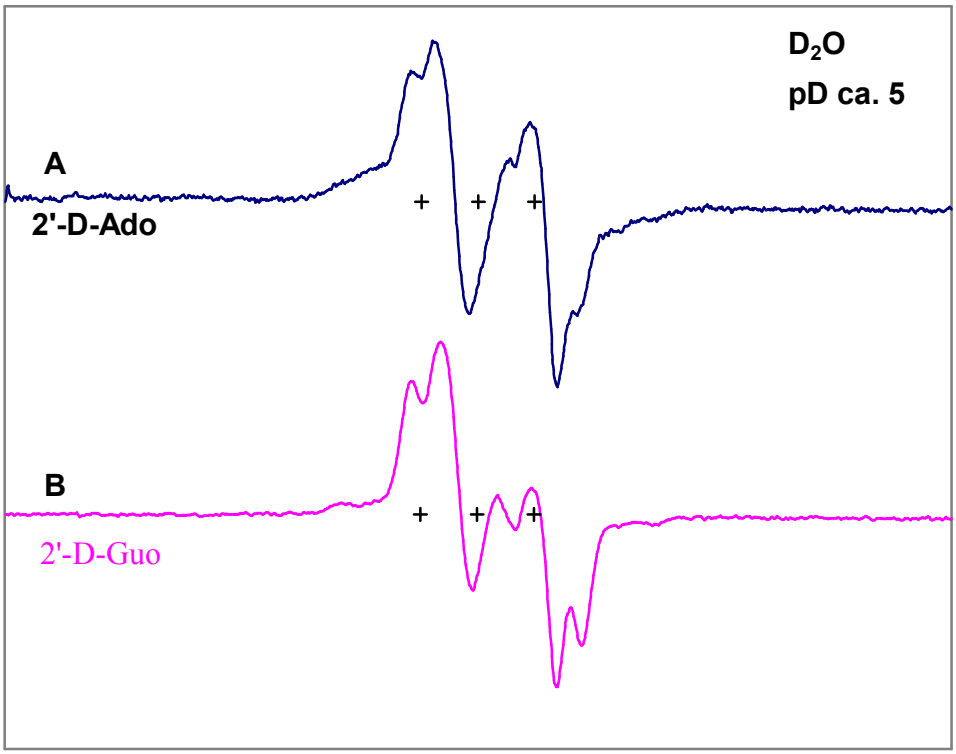

Figure S1. Spectra after visible illumination at 143 K of (A) $A^{\bullet+}$ in 2'-D-Ado, and (B) of $G^{\bullet+}$ in 2'-D-Guo (Ref. 8) in 7.5 M LiCl glass/D_2O in the presence of $K_2S_2O_8$ as an electron scavenger. The central doublet from C5'• is present in both spectra, but the end lines of the quartet belonging to C3'• are lost. The three calibration marks are separated by 26.18 G from 1st to 3rd mark. The center mark is at g=2.0056.

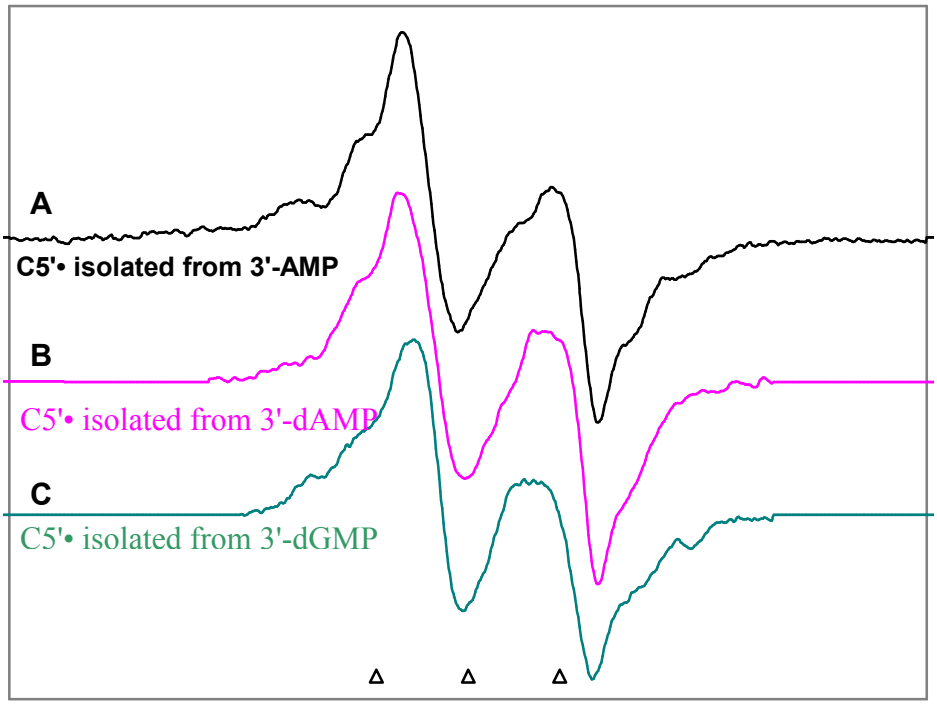

Figure S2. ESR spectra of C5'• isolated from RNA- and DNA- nucleotides. Spectrum (A) C5'• formed via photo-excitation of $A^{\bullet+}$ in glassy (7.5 M $LiCl/D_2O$) sample of 3'-AMP at pD *ca.* 6. Spectra (B) and (C) are the C5'• obtained from glassy (7 M $LiCl/D_2O$) samples of 3'-dAMP (Ref. 9) and 3'-dGMP (Ref. 2) respectively. The hyperfine couplings, total hyperfine splitting, line-shape and g-value of all these three spectra are nearly identical.

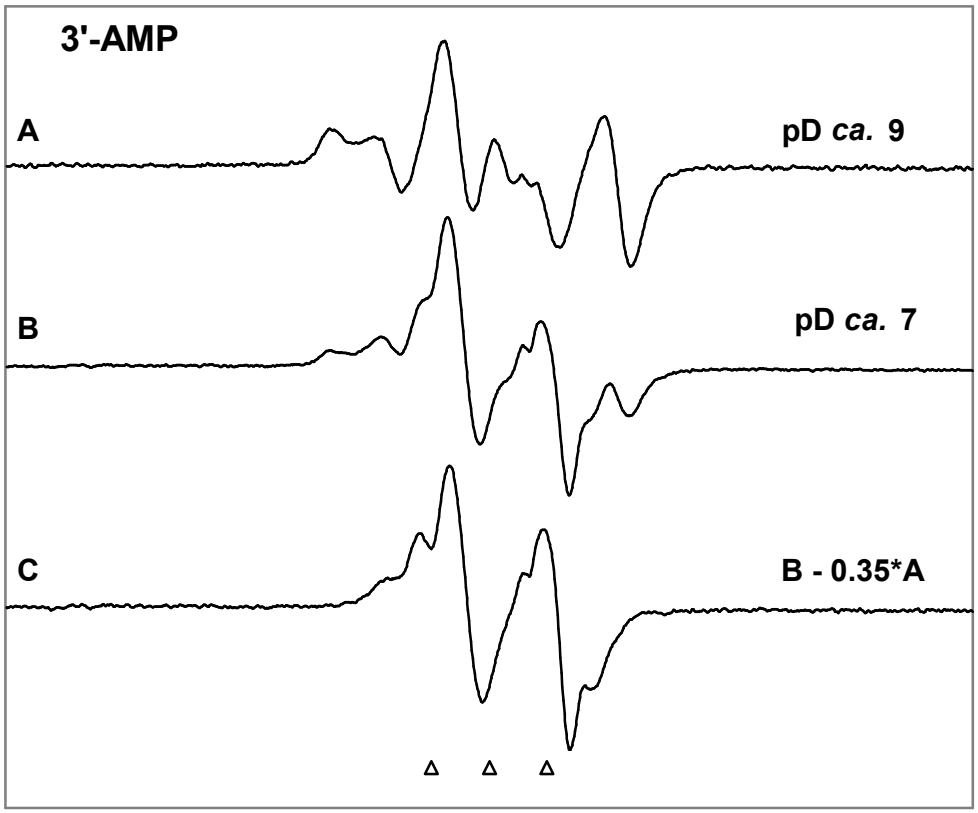

Figure S3. Spectrum (A) is the C5'• formed via photo-excitation of one-electron oxidized adenine in glassy (7.5 M LiCl/D_2O) sample of 3'-AMP at pD *ca.* 9. This spectrum is assigned to C5'• in 3'-AMP with the charge of the phosphate =-2. Spectrum (B) is the C5'• formed via photo-excitation of $A^{\bullet+}$ in glassy (7.5 M LiCl/D_2O) sample of 3'-AMP at pD *ca.* 7. Spectrum (C) shows that in spectrum (B) 35% of spectrum (A) is present.

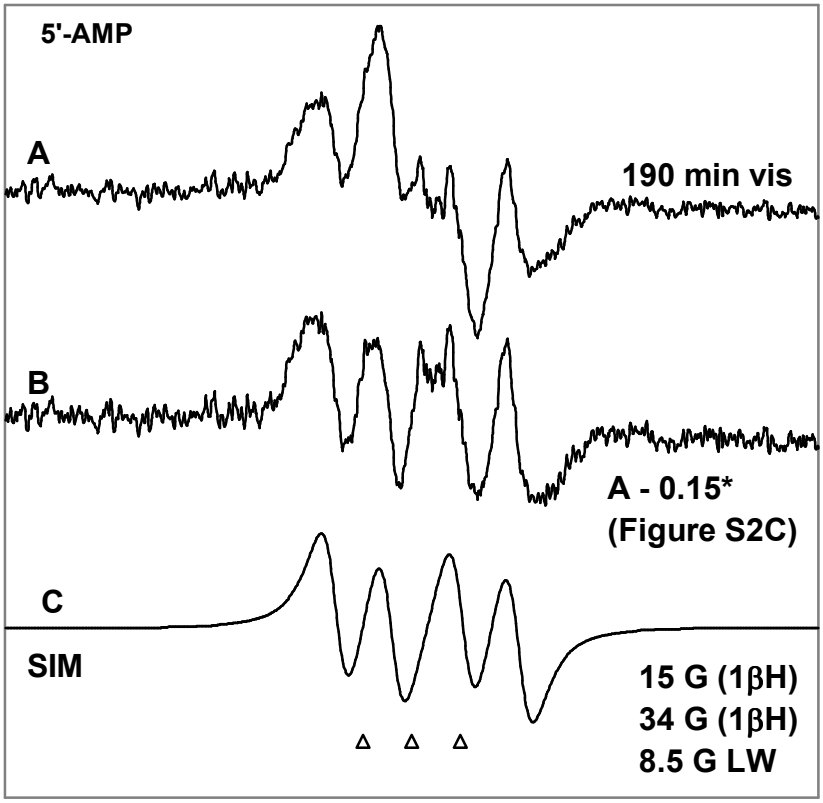

Figure S4. Spectrum (A) represents the sugar radical cohort comprising of C3'• (*ca.* 85%), and C5'• (*ca.* 15%) found in glassy (7.5 M LiCl/D_2O) samples of 5'-AMP via photo-excitation of $A•^+$ followed by subtraction of the remaining ca. 13% of the $A•^+$ spectrum shown in Figure 1A. Spectrum (B) shows the isolation of the quartet owing to careful subtraction of the central doublet (*ca.* 15%) shown in Figure S2C from spectrum A. Spectrum (C) is the isotropic simulation of the quartet with the parameters: 34 G (1βH), 15G (1βH), 8.5G line-width, g(center) = 2.0027.

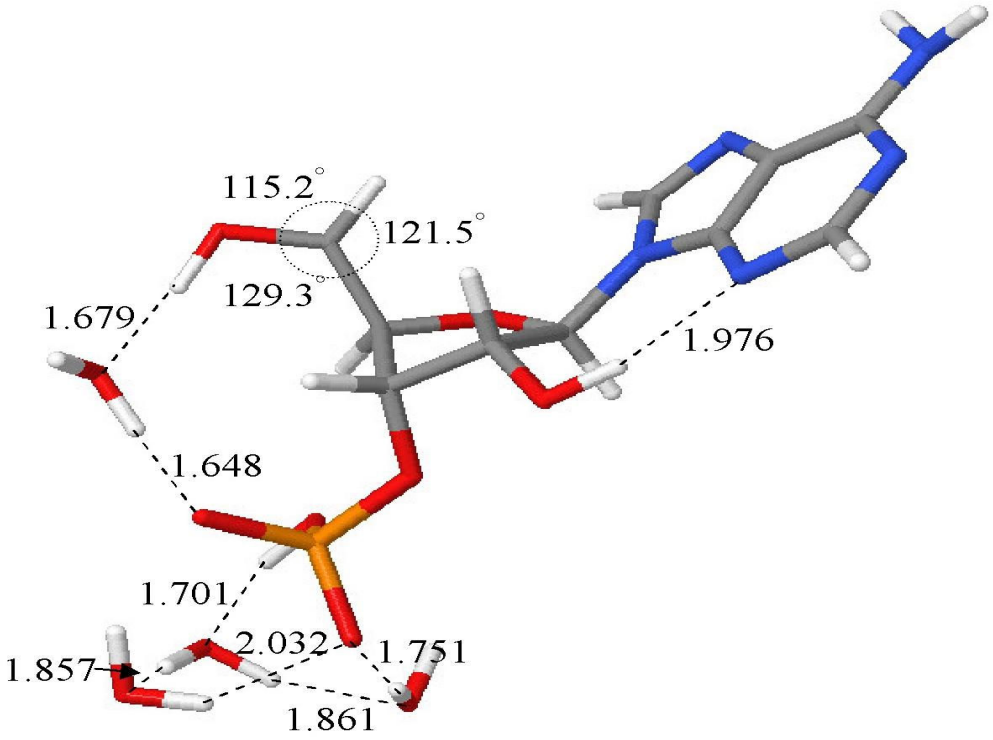

Figure S5. B3LYP/6-31G* optimized geometries of C5'-radical in PO_4H^{-1} in the presence of 4 waters. The atoms O5', C5', H5', and C4' are constrained in the same plane.

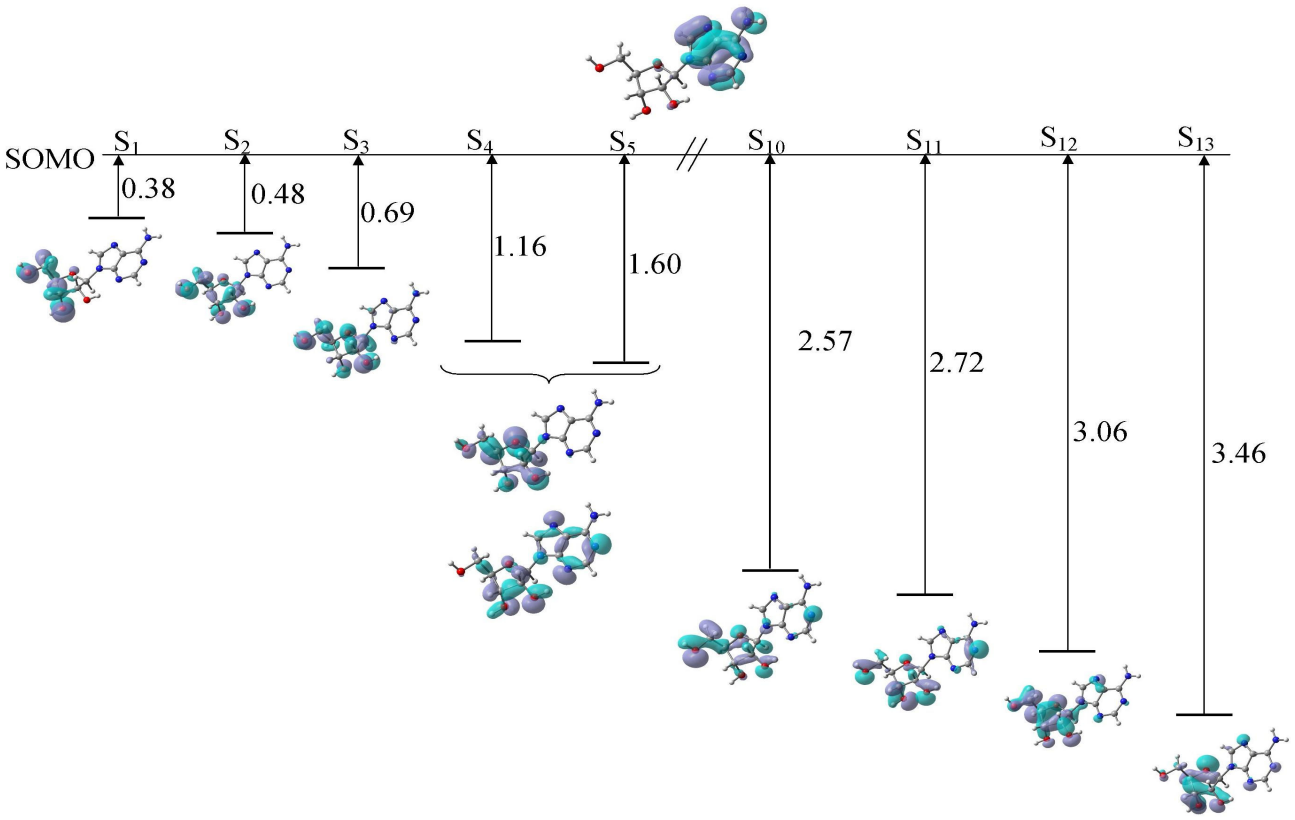

Figure S6. TD-B3LYP/6-31G(d) calculated electronic transitions from inner core molecular orbitals to 70 β SOMO (singly occupied molecular orbital) in Ado cation radical.

Table T1
TD-DFT 6-31/G(d) Calculation for Adenosine cation radical
(Structure Optimized at DFT B3LYP 6-31G*)
Method: TD-DFT
Basis Set: 6-31G(d)
Functionals: B3LYP
Transitions: 13

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Excited State   1:   Spin  -A      0.3779 eV 3280.81 nm  f=0.0006
     68B -> 70B        0.28478
     69B -> 70B        0.94606
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:   Spin  -A      0.4839 eV 2562.21 nm  f=0.0081
     67B -> 70B        0.37271
     68B -> 70B        0.82429
     69B -> 70B       -0.27057

 Excited State   3:   Spin  -A      0.6937 eV 1787.35 nm  f=0.0060
     67B -> 70B        0.86869
     68B -> 70B       -0.44240

 Excited State   4:   Spin  -A      1.1605 eV 1068.36 nm  f=0.0019
     64B -> 70B       -0.38883
     65B -> 70B       -0.57383
     66B -> 70B        0.70734
     67B -> 70B        0.10613

 Excited State   5:   Spin  -A      1.2785 eV  969.73 nm  f=0.0083
     64B -> 70B        0.41515
     65B -> 70B        0.57271
     66B -> 70B        0.68575

 Excited State   6:   Spin  -A      1.6919 eV  732.83 nm  f=0.0014
     60B -> 70B       -0.18752
     62B -> 70B       -0.11232
     63B -> 70B        0.62738
     64B -> 70B        0.62665
     65B -> 70B       -0.42332

 Excited State   7:   Spin  -A      2.0217 eV  613.26 nm  f=0.0141
     59B -> 70B       -0.33712
     61B -> 70B       -0.33321
     62B -> 70B       -0.39537
     63B -> 70B        0.58250
     64B -> 70B       -0.43155
     65B -> 70B        0.28723

 Excited State   8:   Spin  -A      2.1608 eV  573.80 nm  f=0.0099
     59B -> 70B        0.71644
     60B -> 70B        0.25932
     61B -> 70B        0.30289
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     62B -> 70B        0.17837
     63B -> 70B        0.42237
     64B -> 70B       -0.22039
     65B -> 70B        0.23896

Excited State   9:   Spin  -A      2.3964 eV  517.38 nm  f=0.0173
     66A -> 71A       -0.10525
     67A -> 71A        0.12793
     59B -> 70B       -0.31049
     60B -> 70B        0.88293
     62B -> 70B        0.12131
     64B -> 70B        0.13464
     65B -> 70B       -0.15332

Excited State  10:   Spin  -A      2.5743 eV  481.62 nm  f=0.0012
     59B -> 70B       -0.42523
     60B -> 70B       -0.23533
     61B -> 70B        0.25107
     62B -> 70B        0.76395
     63B -> 70B        0.28287
     64B -> 70B       -0.17322

Excited State  11:   Spin  -A      2.7176 eV  456.23 nm  f=0.0007
     56B -> 70B       -0.22676
     59B -> 70B       -0.24155
     61B -> 70B        0.82944
     62B -> 70B       -0.43209

Excited State  12:   Spin  -A      3.0578 eV  405.47 nm  f=0.0003
     56B -> 70B        0.80276
     57B -> 70B       -0.21789
     58B -> 70B        0.47353
     59B -> 70B       -0.11957
     61B -> 70B        0.19459

Excited State  13:   Spin  -A      3.4545 eV  358.91 nm  f=0.0004
     56B -> 70B       -0.48916
     58B -> 70B        0.86210
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Complete reference of the reference no. 31a in the text:

31a. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M.A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.;Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.;Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.;Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.;Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.;Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.;Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels,A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.;Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.;Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian03, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.