## Supporting Information

# Long Living Excited State of Protonated Adenosine Unveiled by Ultrafast Fluorescence Spectroscopy and Density Functional Theoretical Study

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**Global analysis of the kinetic decays of fluorescence intensities** from fs-TRF (F(t), Eq.1) was conducted by simulation with bi-exponential functions (f(t), Eq.2) after deconvolution of the instrumental response function (IRF) ((g(t), Eq.3) of the experimental decay profile. Below shown the relevance equations (Eq.1-4):

$$F(t) = \int_{-\infty}^{t} g(\tau) f(t-\tau) d\tau \qquad \text{Eq.1}$$

$$f(t-\tau) = \sum_{i} a_i e^{-\frac{t}{\tau_i}} \qquad \text{Eq.2}$$

$$g(\tau) = \frac{1}{\pi^{1/2}\sigma} \exp[-\{(t-\tau_0)/\sigma\}^2] \qquad \text{Eq.3}$$

$$\sum_{i} a_i = 1 \qquad \text{Eq.4}$$

In the equations above, IRF ($g(\tau)$) is represented by the Gaussian function, $\tau_i$ represents the time constant of the exponential function and $a_i$ represents the corresponding pre-exponential factor representing percentage contribution of the associated time constant, t represents the delay time after the photoexcitation.[1-3]

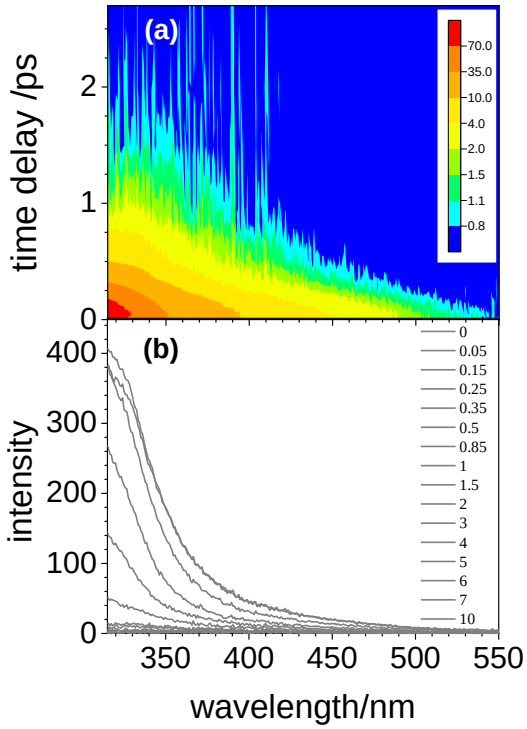


**Fig. S1** (a) 3D and (b) 2D fs-TRF spectra of Ado at pH7 condition after excitation at 267 nm.

**Table S1** Decay kinetic parameters derived from the fs-TRF measurement of adenosine in pH3 condition after excitation at 267 nm.

| Probe /nm | wavelength | $a_1$ | $\tau_1$ (ps) | $a_2$ | $\tau_2$ (ps) |
|---|---|---|---|---|---|
| | 360 | 0.99 | 0.5±0.06 | 0.01 | 2114±11 |
| | 381 | 0.97 | | 0.03 | 2933±12 |

**Table S2** Cartesian coordinates (Å) of DFT optimized adenosine and protonated conformers at ground state ($S_0$) by 6-311G++ (d,p) basis set.

| Neutral adenosine at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.348991 | -1.03178 | -0.4004 |
| 2 | 1.117105 | -2.14391 | -0.68774 |
| 3 | 2.403894 | -1.94434 | -0.55637 |
| 4 | 2.503733 | -0.6204 | -0.16815 |
| 5 | 3.613397 | 0.201244 | 0.123359 |
| 6 | 4.881464 | -0.24422 | 0.067254 |
| 7 | 5.643227 | 0.383205 | 0.270704 |
| 8 | 5.084298 | -1.19261 | -0.20356 |
| 9 | 3.38637 | 1.484389 | 0.473153 |
| 10 | 2.125076 | 1.923153 | 0.526328 |
| 11 | 1.998083 | 2.963546 | 0.808893 |
| 12 | 1.001971 | 1.244854 | 0.2727 |
| 13 | 1.242902 | -0.03165 | -0.06836 |
| 14 | -1.1025 | -0.97229 | -0.46455 |
| 15 | -2.69173 | 0.732924 | -0.86902 |
| 16 | -3.11463 | -0.01615 | 0.398609 |
| 17 | -1.80285 | -0.67074 | 0.871304 |
| 18 | -1.4897 | 0.058215 | -1.35054 |
| 19 | -2.39631 | 2.216272 | -0.68022 |
| 20 | -3.46334 | 0.619811 | -1.63554 |
| 21 | -1.55297 | 2.498289 | 0.427191 |
| 22 | -0.66768 | 2.096002 | 0.282943 |
| 23 | -4.06527 | -1.01912 | 0.044922 |
| 24 | -2.00703 | -1.87956 | 1.587769 |
| 25 | -1.9703 | -1.69894 | 2.533678 |
| 26 | 0.653243 | -3.07246 | -0.98647 |
| 27 | -1.97057 | 2.603969 | -1.6143 |
| 28 | -3.3419 | 2.736387 | -0.5036 |
| 29 | -3.52873 | 0.657818 | 1.153404 |
| 30 | -3.99169 | -1.72203 | 0.706766 |
| 31 | -1.42895 | -1.95305 | -0.82558 |
| 32 | -1.21997 | 0.042689 | 1.454297 |

| *Syn*-N1 at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.336019 | -1.01816 | -0.41639 |
| 2 | 1.090473 | -2.14317 | -0.69013 |
| 3 | 0.617959 | -3.06885 | -0.98239 |
| 4 | 2.380024 | -1.95718 | -0.55647 |
| 5 | 2.487533 | -0.6409 | -0.18364 |
| 6 | 3.626641 | 0.134416 | 0.102903 |
| 7 | 4.869811 | -0.31557 | 0.063126 |
| 8 | 5.672939 | 0.259317 | 0.272698 |
| 9 | 5.032963 | -1.27985 | -0.18949 |
| 10 | 3.342497 | 1.43007 | 0.439241 |
| 11 | 2.073639 | 1.940252 | 0.496826 |
| 12 | 2.008295 | 2.983607 | 0.77526 |
| 13 | 0.996149 | 1.256036 | 0.241235 |
| 14 | 1.233656 | -0.03421 | -0.0924 |
| 15 | -1.12372 | -0.95146 | -0.4742 |
| 16 | -2.74668 | 0.71595 | -0.85081 |
| 17 | -3.14392 | -0.05645 | 0.413197 |
| 18 | -1.44795 | -1.92197 | -0.86325 |
| 19 | -1.81515 | -0.68838 | 0.873292 |
| 20 | -1.50136 | 0.107431 | -1.3204 |
| 21 | -2.52123 | 2.209287 | -0.66194 |
| 22 | -3.50383 | 0.562418 | -1.62418 |
| 23 | -3.56619 | 0.60042 | 1.178211 |
| 24 | -4.07364 | -1.07415 | 0.052116 |
| 25 | -4.00374 | -1.77241 | 0.719054 |
| 26 | -1.2451 | 0.032787 | 1.460462 |
| 27 | -1.98443 | -1.90919 | 1.572474 |
| 28 | -1.9296 | -1.74579 | 2.520709 |
| 29 | 4.10323 | 2.06214 | 0.666755 |
| 30 | -2.1341 | 2.625523 | -1.59958 |
| 31 | -3.48361 | 2.683875 | -0.4554 |
| 32 | -1.66367 | 2.518439 | 0.43027 |
| 33 | -0.7755 | 2.160084 | 0.251759 |

| *Syn*-N3 at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.351573 | -1.05373 | -0.41631 |
| 2 | 1.119265 | -2.19012 | -0.6322 |
| 3 | 0.652075 | -3.12526 | -0.90105 |
| 4 | 2.400664 | -1.99006 | -0.47531 |
| 5 | 2.504797 | -0.65533 | -0.14613 |
| 6 | 3.624505 | 0.16343 | 0.131504 |
| 7 | 4.872677 | -0.29106 | 0.12245 |
| 8 | 5.638095 | 0.334323 | 0.327113 |
| 9 | 5.07093 | -1.25766 | -0.08743 |
| 10 | 3.417516 | 1.478549 | 0.421695 |
| 11 | 2.198868 | 1.955138 | 0.435311 |
| 12 | 2.045748 | 3.002065 | 0.665718 |
| 13 | 1.076041 | 1.244558 | 0.178498 |
| 14 | 1.245396 | -0.07027 | -0.10866 |
| 15 | -1.10406 | -0.96601 | -0.50353 |
| 16 | -2.67064 | 0.763417 | -0.82649 |
| 17 | 0.143745 | 1.703227 | 0.214398 |
| 18 | -3.11142 | -0.0497 | 0.408436 |
| 19 | -1.43726 | -1.89858 | -0.96918 |
| 20 | -1.82014 | -0.75843 | 0.852069 |
| 21 | -1.42507 | 0.162491 | -1.28739 |
| 22 | -2.43273 | 2.241528 | -0.58991 |
| 23 | -3.37224 | 2.715182 | -0.29291 |
| 24 | -3.41582 | 0.653562 | -1.61792 |
| 25 | -1.44968 | 2.388545 | 0.45204 |
| 26 | -1.44186 | 3.302253 | 0.760802 |
| 27 | -3.52141 | 0.583766 | 1.195363 |
| 28 | -4.02954 | -1.08768 | 0.062157 |
| 29 | -1.23216 | -0.08392 | 1.475655 |
| 30 | -2.02338 | -1.94559 | 1.573941 |
| 31 | -2.07633 | 2.708196 | -1.51264 |
| 32 | -4.93351 | -0.76614 | 0.147496 |
| 33 | -2.85101 | -2.33289 | 1.24905 |

| *Syn*-N7 at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.338214 | -1.03396 | -0.39922 |
| 2 | 1.041021 | -2.14511 | -0.66002 |
| 3 | 2.338335 | -1.91006 | -0.51442 |
| 4 | 2.513712 | -0.58121 | -0.15016 |
| 5 | 3.623113 | 0.252865 | 0.131763 |
| 6 | 4.903172 | -0.13314 | 0.090883 |
| 7 | 5.616621 | 0.548468 | 0.303205 |
| 8 | 5.197311 | -1.05888 | -0.17447 |
| 9 | 3.349884 | 1.529091 | 0.465536 |
| 10 | 2.086638 | 1.947513 | 0.507798 |
| 11 | 1.938783 | 2.98606 | 0.783339 |
| 12 | 0.977708 | 1.245134 | 0.247996 |
| 13 | 1.243975 | -0.01982 | -0.07536 |
| 14 | -1.13334 | -0.96238 | -0.46671 |
| 15 | -2.71587 | 0.733539 | -0.86414 |
| 16 | -3.13441 | -0.02193 | 0.401648 |
| 17 | -1.81891 | -0.67181 | 0.877829 |
| 18 | -1.49111 | 0.0754 | -1.33399 |
| 19 | -2.44482 | 2.220161 | -0.68153 |
| 20 | -3.47359 | 0.598304 | -1.63961 |
| 21 | -1.60805 | 2.513811 | 0.428405 |
| 22 | -0.72115 | 2.130841 | 0.275 |
| 23 | -4.07588 | -1.02738 | 0.039506 |
| 24 | -2.01175 | -1.88099 | 1.587762 |
| 25 | -1.94223 | -1.71244 | 2.534161 |
| 26 | 0.613831 | -3.09188 | -0.94701 |
| 27 | 3.050884 | -2.61625 | -0.6524 |
| 28 | -2.02304 | 2.613812 | -1.61423 |
| 29 | -3.3986 | 2.7245 | -0.50635 |
| 30 | -3.55014 | 0.647191 | 1.159303 |
| 31 | -4.03994 | -1.7124 | 0.722436 |
| 32 | -1.45377 | -1.94173 | -0.83579 |
| 33 | -1.23848 | 0.047197 | 1.456819 |

| *Anti*-N1 at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.327911 | 0.135383 | -0.06512 |
| 2 | 0.499486 | 1.451008 | 0.326229 |
| 3 | -0.35539 | 2.092979 | 0.484212 |
| 4 | 1.759503 | 1.79386 | 0.45349 |
| 5 | 2.453572 | 0.653076 | 0.129313 |
| 6 | 3.83482 | 0.396701 | 0.084652 |
| 7 | 4.778539 | 1.27982 | 0.376597 |
| 8 | 5.763842 | 1.06646 | 0.328984 |
| 9 | 4.509804 | 2.212877 | 0.653156 |
| 10 | 4.147763 | -0.87999 | -0.29585 |
| 11 | 3.211428 | -1.83294 | -0.61068 |
| 12 | 3.617007 | -2.79409 | -0.89796 |
| 13 | 1.926714 | -1.63864 | -0.57822 |
| 14 | 1.583421 | -0.38798 | -0.20251 |
| 15 | -0.94167 | -0.54701 | -0.31956 |
| 16 | -3.06653 | 0.306056 | -0.91047 |
| 17 | -3.25261 | -0.61713 | 0.304312 |
| 18 | -0.67748 | -1.5403 | -0.69088 |
| 19 | -1.8506 | -0.6576 | 0.930268 |
| 20 | -1.66504 | 0.187207 | -1.28523 |
| 21 | -3.42494 | 1.764061 | -0.68233 |
| 22 | -3.66176 | -0.0628 | -1.74913 |
| 23 | -4.00379 | -0.24278 | 1.000997 |
| 24 | -3.54654 | -1.96112 | -0.08653 |
| 25 | -4.49955 | -2.07468 | -0.16765 |
| 26 | -1.71311 | 0.221695 | 1.558469 |
| 27 | -1.59543 | -1.79647 | 1.716205 |
| 28 | -2.09437 | -2.52715 | 1.320289 |
| 29 | 5.123156 | -1.15475 | -0.35153 |
| 30 | -3.15517 | 2.337458 | -1.57554 |
| 31 | -4.50875 | 1.837512 | -0.53632 |
| 32 | -2.72135 | 2.25254 | 0.464546 |
| 33 | -2.97886 | 3.167768 | 0.619333 |

| *Anti*-N3 at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | -0.31812 | -0.43588 | -0.50726 |
| 2 | -0.68867 | -1.76433 | -0.6649 |
| 3 | 0.045924 | -2.5076 | -0.92593 |
| 4 | -1.96624 | -1.97114 | -0.46543 |
| 5 | -2.48031 | -0.72779 | -0.16974 |
| 6 | -3.78784 | -0.28345 | 0.136801 |
| 7 | -4.83596 | -1.09651 | 0.191352 |
| 8 | -5.74877 | -0.72673 | 0.412938 |
| 9 | -4.73666 | -2.0845 | 0.012998 |
| 10 | -3.98869 | 1.042742 | 0.389041 |
| 11 | -2.98149 | 1.874711 | 0.354044 |
| 12 | -3.1496 | 2.92275 | 0.567031 |
| 13 | -1.7025 | 1.531237 | 0.06732 |
| 14 | -1.46639 | 0.220462 | -0.1965 |
| 15 | 1.006369 | 0.165513 | -0.77344 |
| 16 | 3.203715 | -0.59105 | -0.40871 |
| 17 | -0.9329 | 2.204409 | 0.114798 |
| 18 | 3.084581 | 0.823899 | 0.168721 |
| 19 | 0.892486 | 0.82481 | -1.64096 |
| 20 | 1.572336 | 0.94619 | 0.420957 |
| 21 | 1.910839 | -0.86668 | -1.03802 |
| 22 | 3.54115 | -1.68255 | 0.587731 |
| 23 | 4.579804 | -1.54226 | 0.910069 |
| 24 | 3.955549 | -0.59897 | -1.20014 |
| 25 | 2.645142 | -1.60746 | 1.697522 |
| 26 | 2.848367 | -2.32312 | 2.309101 |
| 27 | 3.662211 | 0.944978 | 1.088865 |
| 28 | 3.511728 | 1.745587 | -0.82844 |
| 29 | 1.316768 | 0.439148 | 1.352736 |
| 30 | 1.072041 | 2.280773 | 0.395411 |
| 31 | 3.462649 | -2.65252 | 0.085474 |
| 32 | 3.137952 | 2.611139 | -0.61484 |
| 33 | 1.208094 | 2.687833 | 1.261122 |

| *Anti*-N7 at ground state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | -0.2712 | -0.40429 | -0.62182 |
| 2 | -0.59406 | -1.6909 | -0.7792 |
| 3 | -1.89109 | -1.86246 | -0.52728 |
| 4 | -2.44991 | -0.63531 | -0.19135 |
| 5 | -3.72992 | -0.1523 | 0.174974 |
| 6 | -4.83449 | -0.90158 | 0.269566 |
| 7 | -5.69746 | -0.45413 | 0.540557 |
| 8 | -4.85076 | -1.89074 | 0.082775 |
| 9 | -3.82538 | 1.165347 | 0.444498 |
| 10 | -2.74823 | 1.94597 | 0.362985 |
| 11 | -2.89984 | 2.992782 | 0.602321 |
| 12 | -1.50399 | 1.591933 | 0.022265 |
| 13 | -1.41567 | 0.289411 | -0.24987 |
| 14 | 1.061509 | 0.216293 | -0.86136 |
| 15 | 3.158125 | -0.66479 | -0.26252 |
| 16 | 3.066514 | 0.747198 | 0.322693 |
| 17 | 1.555021 | 1.004751 | 0.376851 |
| 18 | 1.980775 | -0.7978 | -1.12324 |
| 19 | 3.212502 | -1.80168 | 0.739863 |
| 20 | 4.030678 | -0.73563 | -0.91372 |
| 21 | 2.107284 | -1.69452 | 1.638568 |
| 22 | 2.123005 | -2.44555 | 2.241196 |
| 23 | 3.700703 | 1.647811 | -0.58039 |
| 24 | 1.283695 | 2.387235 | 0.31817 |
| 25 | 0.313973 | 2.488784 | 0.279228 |
| 26 | 0.095164 | -2.46478 | -1.06927 |
| 27 | -2.35417 | -2.76053 | -0.58306 |
| 28 | 3.181357 | -2.75082 | 0.194478 |
| 29 | 4.166587 | -1.74203 | 1.276964 |
| 30 | 3.520724 | 0.810271 | 1.315219 |
| 31 | 3.290322 | 2.51511 | -0.45639 |
| 32 | 0.93958 | 0.873973 | -1.72621 |
| 33 | 1.149032 | 0.546927 | 1.281949 |

**Table S3** Cartesian coordinates (Å) of DFT optimized adenosine and protonated conformers at excited state ($S_1$) by 6-311G++ (d,p) basis set.

| Neutral adenosine at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | -3.6012 | 1.133861 | 0.078291 |
| 2 | -4.28557 | 0.01523 | -0.02567 |
| 3 | -5.36492 | 0.067523 | -0.05228 |
| 4 | -3.58534 | -1.1915 | -0.0957 |
| 5 | -4.12033 | -2.12434 | -0.18443 |
| 6 | -2.13793 | -1.14184 | -0.04501 |
| 7 | -1.45744 | -2.27595 | -0.09186 |
| 8 | -0.42137 | -2.26273 | -0.04748 |
| 9 | -1.93742 | -3.16172 | -0.16202 |
| 10 | -1.48365 | 0.015681 | 0.045476 |
| 11 | -2.15209 | 1.17791 | 0.114381 |
| 12 | -1.65471 | 2.28768 | 0.207073 |
| 13 | -4.07492 | 2.032679 | 0.135025 |
| 14 | 3.417683 | -1.28099 | 0.105734 |
| 15 | 4.275715 | -0.15702 | 0.102104 |
| 16 | 5.32704 | -0.35649 | 0.199527 |
| 17 | 3.7006 | 1.102166 | 0.003337 |
| 18 | 4.329484 | 1.981232 | -0.00406 |
| 19 | 2.332491 | 1.236929 | -0.09248 |
| 20 | 1.626014 | 2.412968 | -0.32689 |
| 21 | 0.709226 | 2.462674 | 0.105132 |
| 22 | 2.161957 | 3.248307 | -0.135 |
| 23 | 1.546253 | 0.064471 | -0.08312 |
| 24 | 2.065005 | -1.19854 | 0.026955 |
| 25 | 1.33613 | -2.20697 | 0.047266 |
| 26 | 3.798947 | -2.21138 | 0.178463 |
| 27 | 0.530046 | 0.128246 | -0.08866 |

| *Syn*-N1 at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.309847 | -1.06977 | -0.30702 |
| 2 | 1.084947 | -2.17588 | -0.59805 |
| 3 | 0.637484 | -3.09762 | -0.93868 |
| 4 | 2.374434 | -1.98312 | -0.41581 |
| 5 | 2.485401 | -0.72565 | 0.094517 |
| 6 | 3.609893 | 0.140913 | 0.021131 |
| 7 | 4.810974 | -0.27551 | -0.32681 |
| 8 | 5.610112 | 0.343233 | -0.38466 |
| 9 | 4.957759 | -1.25812 | -0.52426 |
| 10 | 3.369107 | 1.464586 | 0.296933 |
| 11 | 2.152196 | 1.783931 | 0.894454 |
| 12 | 2.089589 | 2.664718 | 1.512569 |
| 13 | 1.004428 | 1.165654 | 0.404252 |
| 14 | 1.181072 | -0.09842 | 0.153738 |
| 15 | -1.13623 | -0.97149 | -0.44603 |
| 16 | -2.66036 | 0.761897 | -0.93929 |
| 17 | -3.16755 | 0.025797 | 0.305712 |
| 18 | -1.46931 | -1.9391 | -0.83498 |
| 19 | -1.8994 | -0.65775 | 0.854142 |
| 20 | -1.43216 | 0.079085 | -1.33713 |
| 21 | -2.36836 | 2.247514 | -0.75472 |
| 22 | -3.38058 | 0.644536 | -1.75318 |
| 23 | -3.60546 | 0.71037 | 1.037114 |
| 24 | -4.11763 | -0.95377 | -0.10202 |
| 25 | -4.12377 | -1.64411 | 0.576724 |
| 26 | -1.336 | 0.046846 | 1.467118 |
| 27 | -2.16837 | -1.85815 | 1.555472 |
| 28 | -2.14299 | -1.6884 | 2.503852 |
| 29 | 4.138288 | 2.123281 | 0.33604 |
| 30 | -1.90912 | 2.628883 | -1.67391 |
| 31 | -3.31847 | 2.767404 | -0.60896 |
| 32 | -1.56317 | 2.53607 | 0.379726 |
| 33 | -0.6681 | 2.174054 | 0.242377 |

| *Syn*-N3 at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.340775 | -1.05366 | -0.42602 |
| 2 | 1.105517 | -2.17712 | -0.66286 |
| 3 | 0.664789 | -3.11857 | -0.94974 |
| 4 | 2.423262 | -1.94552 | -0.4979 |
| 5 | 2.514922 | -0.65729 | -0.15959 |
| 6 | 3.663861 | 0.201974 | 0.137585 |
| 7 | 4.894505 | -0.33126 | 0.099384 |
| 8 | 5.70547 | 0.237062 | 0.308724 |
| 9 | 5.026772 | -1.30599 | -0.13639 |
| 10 | 3.473153 | 1.477296 | 0.445641 |
| 11 | 2.248312 | 1.991125 | 0.488487 |
| 12 | 2.079753 | 3.025761 | 0.736529 |
| 13 | 1.054904 | 1.226996 | 0.193598 |
| 14 | 1.227881 | -0.05339 | -0.10596 |
| 15 | -1.11703 | -0.97442 | -0.49643 |
| 16 | -2.69842 | 0.735441 | -0.83721 |
| 17 | 0.130523 | 1.689949 | 0.209238 |
| 18 | -3.11738 | -0.05439 | 0.419926 |
| 19 | -1.45069 | -1.9209 | -0.93294 |
| 20 | -1.81336 | -0.73872 | 0.866829 |
| 21 | -1.45368 | 0.131328 | -1.30111 |
| 22 | -2.4711 | 2.22017 | -0.63529 |
| 23 | -3.41712 | 2.692246 | -0.35594 |
| 24 | -3.45066 | 0.601367 | -1.61801 |
| 25 | -1.49602 | 2.400076 | 0.406757 |
| 26 | -1.48408 | 3.32516 | 0.678899 |
| 27 | -3.5257 | 0.591956 | 1.197143 |
| 28 | -4.0253 | -1.11115 | 0.107152 |
| 29 | -1.22416 | -0.04198 | 1.464055 |
| 30 | -1.99431 | -1.90807 | 1.619939 |
| 31 | -2.11501 | 2.66593 | -1.56862 |
| 32 | -4.93258 | -0.80052 | 0.197792 |
| 33 | -2.81839 | -2.31629 | 1.311544 |

| *Syn*-N7 at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.335339 | -1.03164 | -0.42823 |
| 2 | 1.059956 | -2.1716 | -0.78378 |
| 3 | 2.438209 | -1.89426 | -0.60511 |
| 4 | 2.53143 | -0.58389 | -0.17221 |
| 5 | 3.595484 | 0.276361 | 0.144359 |
| 6 | 4.885274 | -0.08756 | 0.125686 |
| 7 | 5.588276 | 0.59622 | 0.38428 |
| 8 | 5.195594 | -1.00913 | -0.15458 |
| 9 | 3.340227 | 1.572652 | 0.50694 |
| 10 | 2.096513 | 1.972095 | 0.529726 |
| 11 | 1.899608 | 2.999281 | 0.810435 |
| 12 | 0.988355 | 1.219135 | 0.224463 |
| 13 | 1.239983 | -0.03857 | -0.10026 |
| 14 | -1.11244 | -0.95483 | -0.46404 |
| 15 | -2.7515 | 0.698735 | -0.85216 |
| 16 | -3.12926 | -0.04916 | 0.432966 |
| 17 | -1.79376 | -0.66959 | 0.888728 |
| 18 | -1.50837 | 0.093778 | -1.32303 |
| 19 | -2.53744 | 2.19859 | -0.69998 |
| 20 | -3.51759 | 0.524225 | -1.6128 |
| 21 | -1.66057 | 2.537809 | 0.367572 |
| 22 | -0.78238 | 2.156902 | 0.191689 |
| 23 | -4.06263 | -1.07384 | 0.105667 |
| 24 | -1.95744 | -1.87718 | 1.610366 |
| 25 | -1.83608 | -1.70871 | 2.551352 |
| 26 | 0.654074 | -3.16743 | -0.72107 |
| 27 | 3.07764 | -2.62221 | -0.31012 |
| 28 | -2.17056 | 2.596654 | -1.65347 |
| 29 | -3.49884 | 2.670486 | -0.48418 |
| 30 | -3.54125 | 0.621961 | 1.19177 |
| 31 | -3.98886 | -1.75448 | 0.790306 |
| 32 | -1.45334 | -1.92704 | -0.83374 |
| 33 | -1.2199 | 0.061571 | 1.45909 |

| *Anti*-N1 at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | 0.311897 | 0.117558 | -0.16223 |
| 2 | 0.493874 | 1.450891 | 0.16316 |
| 3 | -0.35727 | 2.09771 | 0.326835 |
| 4 | 1.759993 | 1.807632 | 0.230192 |
| 5 | 2.468859 | 0.706887 | -0.15118 |
| 6 | 3.811472 | 0.380513 | 0.173398 |
| 7 | 4.668997 | 1.259654 | 0.650318 |
| 8 | 5.626066 | 1.023024 | 0.878972 |
| 9 | 4.383393 | 2.225414 | 0.75693 |
| 10 | 4.174303 | -0.9416 | -0.00759 |
| 11 | 3.336505 | -1.68437 | -0.8409 |
| 12 | 3.758269 | -2.40277 | -1.52617 |
| 13 | 1.975912 | -1.61775 | -0.58981 |
| 14 | 1.565212 | -0.39901 | -0.40328 |
| 15 | -0.96777 | -0.56472 | -0.3572 |
| 16 | -3.11534 | 0.303516 | -0.8387 |
| 17 | -3.24742 | -0.6277 | 0.376672 |
| 18 | -0.72202 | -1.5575 | -0.74346 |
| 19 | -1.81727 | -0.67985 | 0.934454 |
| 20 | -1.73582 | 0.172044 | -1.28565 |
| 21 | -3.4449 | 1.763777 | -0.58231 |
| 22 | -3.75586 | -0.05222 | -1.649 |
| 23 | -3.96295 | -0.25593 | 1.111338 |
| 24 | -3.56513 | -1.96705 | -0.01072 |
| 25 | -4.52127 | -2.07514 | -0.05356 |
| 26 | -1.64446 | 0.193973 | 1.56149 |
| 27 | -1.53095 | -1.82577 | 1.698554 |
| 28 | -2.0512 | -2.55135 | 1.321113 |
| 29 | 5.146875 | -1.20743 | 0.08793 |
| 30 | -3.22641 | 2.339728 | -1.48777 |
| 31 | -4.51622 | 1.846929 | -0.36714 |
| 32 | -2.66452 | 2.239587 | 0.519926 |
| 33 | -2.92266 | 3.14705 | 0.714644 |

| *Anti*-N3 at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | -0.30461 | -0.40948 | -0.49362 |
| 2 | -0.63915 | -1.73859 | -0.5952 |
| 3 | 0.092355 | -2.49383 | -0.82554 |
| 4 | -1.95969 | -1.94713 | -0.38516 |
| 5 | -2.48075 | -0.73735 | -0.16705 |
| 6 | -3.83955 | -0.28183 | 0.143436 |
| 7 | -4.82863 | -1.18502 | 0.214875 |
| 8 | -5.77481 | -0.89129 | 0.421256 |
| 9 | -4.64416 | -2.16707 | 0.05949 |
| 10 | -4.07066 | 1.009864 | 0.342466 |
| 11 | -3.09301 | 1.904297 | 0.2689 |
| 12 | -3.27428 | 2.956057 | 0.414226 |
| 13 | -1.71685 | 1.548967 | -0.02127 |
| 14 | -1.47018 | 0.256357 | -0.22409 |
| 15 | 1.013951 | 0.209288 | -0.74339 |
| 16 | 3.216123 | -0.56108 | -0.45529 |
| 17 | -0.9589 | 2.22001 | 0.098538 |
| 18 | 3.103869 | 0.817751 | 0.204219 |
| 19 | 0.875454 | 0.918872 | -1.5677 |
| 20 | 1.594183 | 0.928132 | 0.484579 |
| 21 | 1.912096 | -0.80241 | -1.07979 |
| 22 | 3.566738 | -1.70806 | 0.471718 |
| 23 | 4.611012 | -1.58728 | 0.783993 |
| 24 | 3.953971 | -0.52338 | -1.25858 |
| 25 | 2.68904 | -1.69219 | 1.597885 |
| 26 | 2.877151 | -2.45897 | 2.149327 |
| 27 | 3.69326 | 0.886144 | 1.12226 |
| 28 | 3.515165 | 1.796656 | -0.74289 |
| 29 | 1.348782 | 0.375516 | 1.392687 |
| 30 | 1.099281 | 2.261223 | 0.527109 |
| 31 | 3.47759 | -2.64827 | -0.0824 |
| 32 | 3.134217 | 2.645051 | -0.4778 |
| 33 | 1.193341 | 2.608362 | 1.423653 |

| *Anti*-N7 at excited state | | | |
|---|---|---|---|
| Atom | X | Y | Z |
| 1 | -0.28554 | -0.49851 | -0.51358 |
| 2 | -0.69364 | -1.76143 | -0.93179 |
| 3 | -2.06739 | -1.90578 | -0.59097 |
| 4 | -2.51826 | -0.65636 | -0.21433 |
| 5 | -3.75517 | -0.11 | 0.170788 |
| 6 | -4.90301 | -0.79926 | 0.21917 |
| 7 | -5.74814 | -0.31668 | 0.504369 |
| 8 | -4.9626 | -1.78843 | 0.015149 |
| 9 | -3.83502 | 1.211054 | 0.531632 |
| 10 | -2.73959 | 1.921976 | 0.529867 |
| 11 | -2.80919 | 2.963724 | 0.816695 |
| 12 | -1.48327 | 1.484041 | 0.185546 |
| 13 | -1.41282 | 0.209153 | -0.15477 |
| 14 | 1.026841 | 0.086799 | -0.84018 |
| 15 | 3.181124 | -0.67514 | -0.24855 |
| 16 | 3.080325 | 0.796601 | 0.156148 |
| 17 | 1.567719 | 1.027077 | 0.26524 |
| 18 | 1.945159 | -0.96747 | -0.96644 |
| 19 | 3.380172 | -1.65929 | 0.889491 |
| 20 | 4.001921 | -0.80332 | -0.95724 |
| 21 | 2.389867 | -1.43736 | 1.894936 |
| 22 | 2.501536 | -2.09546 | 2.589015 |
| 23 | 3.640063 | 1.589104 | -0.88849 |
| 24 | 1.27568 | 2.394031 | 0.0695 |
| 25 | 0.313953 | 2.500668 | 0.158356 |
| 26 | -0.0181 | -2.60016 | -0.96913 |
| 27 | -2.64091 | -2.57359 | -1.09122 |
| 28 | 3.310146 | -2.6763 | 0.489189 |
| 29 | 4.389445 | -1.5148 | 1.293789 |
| 30 | 3.584433 | 0.998892 | 1.105018 |
| 31 | 3.236421 | 2.466213 | -0.83081 |
| 32 | 0.930779 | 0.62447 | -1.79259 |
| 33 | 1.223575 | 0.671109 | 1.239352 |

**Table S4** Vibration frequency of DFT optimized adenosine and conformers at ground state ($S_0$) by 6-311G++ (d,p) basis set.

| Neutral adenosine at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| （1） | 45.48 | （31） | 734.67 | （61） | 1333.89 |
| （2） | 48.92 | （32） | 752.1 | （62） | 1348.98 |
| （3） | 81.86 | （33） | 799.89 | （63） | 1361.88 |
| （4） | 104.96 | （34） | 808.39 | （64） | 1364.9 |
| （5） | 111.06 | （35） | 850.46 | （65） | 1381.29 |
| （6） | 130.37 | （36） | 862.28 | （66） | 1389.72 |
| （7） | 148.64 | （37） | 869.86 | （67） | 1413.44 |
| （8） | 164.27 | （38） | 900.98 | （68） | 1425.61 |
| （9） | 206.72 | （39） | 916.47 | （69） | 1440.09 |
| （10） | 213.46 | （40） | 926.7 | （70） | 1455.35 |
| （11） | 239.42 | （41） | 974 | （71） | 1457.83 |
| （12） | 246.88 | （42） | 987.96 | （72） | 1484.46 |
| （13） | 250.79 | （43） | 996.69 | （73） | 1495.15 |
| （14） | 276.66 | （44） | 1040.98 | （74） | 1523.31 |
| （15） | 297.97 | （45） | 1049.42 | （75） | 1605.27 |
| （16） | 332.84 | （46） | 1069.47 | （76） | 1608.79 |
| （17） | 339.66 | （47） | 1076.62 | （77） | 1640.42 |
| （18） | 385 | （48） | 1092.31 | （78） | 3005.92 |
| （19） | 418.53 | （49） | 1108.74 | （79） | 3042.77 |
| （20） | 427.29 | （50） | 1122.99 | （80） | 3053.71 |
| （21） | 527.85 | （51） | 1199.95 | （81） | 3059.48 |
| （22） | 530.11 | （52） | 1213.79 | （82） | 3072.61 |
| （23） | 537.54 | （53） | 1221.56 | （83） | 3103.41 |
| （24） | 548.04 | （54） | 1249.97 | （84） | 3169.26 |
| （25） | 571.38 | （55） | 1254.05 | （85） | 3242.98 |
| （26） | 611.58 | （56） | 1271.98 | （86） | 3411.55 |
| （27） | 641.19 | （57） | 1295.7 | （87） | 3596.8 |
| （28） | 658.5 | （58） | 1315.35 | （88） | 3722.96 |
| （29） | 688.47 | （59） | 1324.5 | （89） | 3745.28 |
| （30） | 706.5 | （60） | 1328.93 | （90） | 3831.23 |

| *Syn*-N1 at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 41.2633 | (32) | 710.6702 | (63) | 1349.3308 |
| (2) | 52.7872 | (33) | 729.8902 | (64) | 1360.8851 |
| (3) | 77.7005 | (34) | 747.8715 | (65) | 1380.5197 |
| (4) | 95.8082 | (35) | 784.3645 | (66) | 1387.6524 |
| (5) | 132.6624 | (36) | 850.9322 | (67) | 1410.4955 |
| (6) | 149.9171 | (37) | 865.1717 | (68) | 1421.3627 |
| (7) | 150.6041 | (38) | 889.3059 | (69) | 1428.3066 |
| (8) | 203.3474 | (39) | 902.2905 | (70) | 1439.036 |
| (9) | 207.8357 | (40) | 914.9996 | (71) | 1448.4083 |
| (10) | 228.0589 | (41) | 929.922 | (72) | 1459.7619 |
| (11) | 236.9733 | (42) | 947.4613 | (73) | 1471.6171 |
| (12) | 246.6304 | (43) | 986.4997 | (74) | 1485.9519 |
| (13) | 266.908 | (44) | 997.0842 | (75) | 1523.5348 |
| (14) | 294.1055 | (45) | 1040.0617 | (76) | 1585.8831 |
| (15) | 328.2446 | (46) | 1057.7732 | (77) | 1634.3223 |
| (16) | 334.6789 | (47) | 1073.4702 | (78) | 1648.4066 |
| (17) | 383.2532 | (48) | 1081.3003 | (79) | 1700.3423 |
| (18) | 395.7016 | (49) | 1090.8187 | (80) | 3016.5208 |
| (19) | 410.9244 | (50) | 1111.1079 | (81) | 3047.2524 |
| (20) | 424.577 | (51) | 1125.4883 | (82) | 3056.7938 |
| (21) | 514.9632 | (52) | 1167.3695 | (83) | 3065.8469 |
| (22) | 523.7726 | (53) | 1205.6399 | (84) | 3085.3421 |
| (23) | 535.3914 | (54) | 1213.5851 | (85) | 3096.6109 |
| (24) | 549.0621 | (55) | 1240.7801 | (86) | 3224.7088 |
| (25) | 569.7799 | (56) | 1242.1035 | (87) | 3253.6515 |
| (26) | 611.6474 | (57) | 1260.1061 | (88) | 3565.2778 |
| (27) | 637.1689 | (58) | 1294.148 | (89) | 3574.6353 |
| (28) | 639.5325 | (59) | 1303.849 | (90) | 3598.7164 |
| (29) | 675.1555 | (60) | 1322.4297 | (91) | 3689.4642 |
| (30) | 684.7109 | (61) | 1324.6187 | (92) | 3749.9259 |
| (31) | 705.7081 | (62) | 1348.3082 | (93) | 3827.2227 |

| *Syn*-N3 at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 45.3126 | (32) | 727.2208 | (63) | 1344.856 |
| (2) | 56.8057 | (33) | 738.06 | (64) | 1355.907 |
| (3) | 71.5606 | (34) | 784.3677 | (65) | 1379.7781 |
| (4) | 112.0629 | (35) | 846.0262 | (66) | 1392.4823 |
| (5) | 126.1531 | (36) | 869.6168 | (67) | 1418.074 |
| (6) | 142.0068 | (37) | 873.7856 | (68) | 1420.5008 |
| (7) | 158.8177 | (38) | 894.4801 | (69) | 1425.2368 |
| (8) | 193.9655 | (39) | 902.4526 | (70) | 1438.6383 |
| (9) | 212.4935 | (40) | 917.6401 | (71) | 1446.3115 |
| (10) | 224.3519 | (41) | 928.9237 | (72) | 1478.762 |
| (11) | 248.9891 | (42) | 979.9149 | (73) | 1498.2006 |
| (12) | 264.945 | (43) | 980.6102 | (74) | 1509.0171 |
| (13) | 273.9946 | (44) | 992.3247 | (75) | 1535.6562 |
| (14) | 295.6208 | (45) | 1044.3609 | (76) | 1572.9987 |
| (15) | 324.8783 | (46) | 1059.7897 | (77) | 1632.8908 |
| (16) | 336.7482 | (47) | 1073.5401 | (78) | 1660.3365 |
| (17) | 356.6509 | (48) | 1078.0824 | (79) | 1667.3641 |
| (18) | 380.9625 | (49) | 1089.7847 | (80) | 3039.759 |
| (19) | 394.9159 | (50) | 1117.4529 | (81) | 3052.8879 |
| (20) | 428.3965 | (51) | 1122.9026 | (82) | 3073.4776 |
| (21) | 446.2583 | (52) | 1185.0915 | (83) | 3089.5567 |
| (22) | 516.9332 | (53) | 1198.6234 | (84) | 3093.5575 |
| (23) | 530.7507 | (54) | 1210.9942 | (85) | 3094.1133 |
| (24) | 540.5395 | (55) | 1221.9006 | (86) | 3101.2517 |
| (25) | 543.1884 | (56) | 1251.2516 | (87) | 3213.7726 |
| (26) | 577.702 | (57) | 1264.5307 | (88) | 3255.6655 |
| (27) | 610.027 | (58) | 1269.6431 | (89) | 3578.9662 |
| (28) | 630.4645 | (59) | 1277.8411 | (90) | 3702.6317 |
| (29) | 655.1042 | (60) | 1286.3468 | (91) | 3721.5787 |
| (30) | 679.448 | (61) | 1309.5192 | (92) | 3823.544 |
| (31) | 693.336 | (62) | 1335.6099 | (93) | 3838.1486 |

| *Syn*-N7 at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 39.3722 | (32) | 735.4279 | (63) | 1345.3482 |
| (2) | 52.6664 | (33) | 744.5232 | (64) | 1351.2646 |
| (3) | 79.2115 | (34) | 751 | (65) | 1361.6314 |
| (4) | 102.6795 | (35) | 795.0617 | (66) | 1382.6969 |
| (5) | 130.8786 | (36) | 841.5082 | (67) | 1389.7702 |
| (6) | 145.5346 | (37) | 859.7716 | (68) | 1411.4909 |
| (7) | 158.6327 | (38) | 889.6238 | (69) | 1418.6369 |
| (8) | 195.9386 | (39) | 902.0013 | (70) | 1436.0866 |
| (9) | 206.4524 | (40) | 915.6844 | (71) | 1445.3221 |
| (10) | 225.2966 | (41) | 924.9878 | (72) | 1460.5174 |
| (11) | 234.1616 | (42) | 985.166 | (73) | 1485.0576 |
| (12) | 248.8676 | (43) | 990.1502 | (74) | 1503.3281 |
| (13) | 255.3228 | (44) | 998.0803 | (75) | 1526.688 |
| (14) | 277.4958 | (45) | 1042.6321 | (76) | 1573.8064 |
| (15) | 309.5294 | (46) | 1059.4905 | (77) | 1616.7029 |
| (16) | 332.9791 | (47) | 1066.7586 | (78) | 1634.4444 |
| (17) | 339.9619 | (48) | 1086.7479 | (79) | 1668.2236 |
| (18) | 393.2159 | (49) | 1095.36 | (80) | 3014.1415 |
| (19) | 408.6416 | (50) | 1113.1197 | (81) | 3049.9847 |
| (20) | 423.8408 | (51) | 1124.2091 | (82) | 3060.09 |
| (21) | 509.4707 | (52) | 1166.9363 | (83) | 3072.1916 |
| (22) | 524.1116 | (53) | 1208.2004 | (84) | 3081.5868 |
| (23) | 528.6647 | (54) | 1225.6193 | (85) | 3101.8709 |
| (24) | 546.7798 | (55) | 1244.1093 | (86) | 3186.218 |
| (25) | 559.8552 | (56) | 1250.6325 | (87) | 3283.809 |
| (26) | 579.1742 | (57) | 1258.0128 | (88) | 3512.6705 |
| (27) | 606.6443 | (58) | 1291.3789 | (89) | 3590.7759 |
| (28) | 639.6996 | (59) | 1294.9786 | (90) | 3608.991 |
| (29) | 644.5593 | (60) | 1319.0484 | (91) | 3715.1872 |
| (30) | 690.4975 | (61) | 1325.0679 | (92) | 3753.6827 |
| (31) | 700.6011 | (62) | 1339.335 | (93) | 3828.6763 |

| *Anti*-N1 at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 31.7236 | (32) | 730.1691 | (63) | 1346.1565 |
| (2) | 50.0269 | (33) | 730.7383 | (64) | 1367.2892 |
| (3) | 60.9915 | (34) | 753.3504 | (65) | 1377.9037 |
| (4) | 92.7624 | (35) | 789.9867 | (66) | 1385.0212 |
| (5) | 113.9967 | (36) | 838.6718 | (67) | 1422.1326 |
| (6) | 131.8581 | (37) | 865.2538 | (68) | 1432.952 |
| (7) | 155.3467 | (38) | 892.0925 | (69) | 1437.0206 |
| (8) | 193.7783 | (39) | 915.0003 | (70) | 1446.9023 |
| (9) | 207.4639 | (40) | 924.3188 | (71) | 1448.7161 |
| (10) | 222.9853 | (41) | 925.616 | (72) | 1456.1731 |
| (11) | 234.5185 | (42) | 942.0612 | (73) | 1472.8043 |
| (12) | 241.7738 | (43) | 979.4032 | (74) | 1499.4261 |
| (13) | 260.1933 | (44) | 1006.3617 | (75) | 1527.2384 |
| (14) | 271.2441 | (45) | 1038.0962 | (76) | 1582.8229 |
| (15) | 305.1866 | (46) | 1047.487 | (77) | 1641.4405 |
| (16) | 323.4347 | (47) | 1075.5837 | (78) | 1667.681 |
| (17) | 342.7231 | (48) | 1086.5827 | (79) | 1698.817 |
| (18) | 350.345 | (49) | 1092.0364 | (80) | 3014.7896 |
| (19) | 381.7774 | (50) | 1112.8654 | (81) | 3056.0184 |
| (20) | 431.9402 | (51) | 1119.8487 | (82) | 3070.6759 |
| (21) | 446.9829 | (52) | 1157.4308 | (83) | 3073.7821 |
| (22) | 522.7988 | (53) | 1199.1485 | (84) | 3089.9854 |
| (23) | 524.1582 | (54) | 1204.5611 | (85) | 3116.323 |
| (24) | 539.0329 | (55) | 1206.8261 | (86) | 3224.4743 |
| (25) | 566.3844 | (56) | 1235.405 | (87) | 3238.1781 |
| (26) | 582.6753 | (57) | 1261.221 | (88) | 3573.8919 |
| (27) | 626.2412 | (58) | 1268.1122 | (89) | 3580.2964 |
| (28) | 638.2584 | (59) | 1294.9798 | (90) | 3695.474 |
| (29) | 648.3976 | (60) | 1302.8548 | (91) | 3728.9839 |
| (30) | 683.1459 | (61) | 1319.4174 | (92) | 3831.6261 |
| (31) | 689.7946 | (62) | 1342.0013 | (93) | 3838.4232 |

| *Anti*-N3 at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 24.1756 | (32) | 731.9203 | (63) | 1346.0432 |
| (2) | 38.7379 | (33) | 754.0723 | (64) | 1359.0402 |
| (3) | 71.0671 | (34) | 766.2872 | (65) | 1365.3712 |
| (4) | 106.6485 | (35) | 793.0263 | (66) | 1384.3586 |
| (5) | 108.3211 | (36) | 850.6839 | (67) | 1400.7063 |
| (6) | 129.805 | (37) | 863.9809 | (68) | 1409.6727 |
| (7) | 160.6561 | (38) | 881.4629 | (69) | 1419.5739 |
| (8) | 187.1431 | (39) | 906.1496 | (70) | 1441.3026 |
| (9) | 197.1745 | (40) | 920.8553 | (71) | 1451.7712 |
| (10) | 203.0454 | (41) | 922.3183 | (72) | 1471.7988 |
| (11) | 214.2734 | (42) | 963.5593 | (73) | 1498.755 |
| (12) | 254.1989 | (43) | 982.7775 | (74) | 1502.3611 |
| (13) | 261.2238 | (44) | 992.4351 | (75) | 1528.6303 |
| (14) | 293.2542 | (45) | 1037.3853 | (76) | 1554.0336 |
| (15) | 312.5321 | (46) | 1054.7704 | (77) | 1632.9025 |
| (16) | 323.7791 | (47) | 1072.8446 | (78) | 1650.9773 |
| (17) | 349.5059 | (48) | 1081.3211 | (79) | 1660.8422 |
| (18) | 362.2819 | (49) | 1105.5896 | (80) | 3013.4031 |
| (19) | 402.5355 | (50) | 1117.3119 | (81) | 3030.2441 |
| (20) | 406.4548 | (51) | 1118.2728 | (82) | 3055.3265 |
| (21) | 477.0634 | (52) | 1173.2117 | (83) | 3060.3792 |
| (22) | 526.2315 | (53) | 1205.6012 | (84) | 3085.5381 |
| (23) | 530.7013 | (54) | 1206.0637 | (85) | 3100.3654 |
| (24) | 542.5398 | (55) | 1214.914 | (86) | 3217.6567 |
| (25) | 561.2835 | (56) | 1229.0572 | (87) | 3283.2851 |
| (26) | 579.0203 | (57) | 1243.079 | (88) | 3409.6785 |
| (27) | 619.3234 | (58) | 1265.0688 | (89) | 3577.4972 |
| (28) | 633.577 | (59) | 1276.1224 | (90) | 3701.0945 |
| (29) | 649.3146 | (60) | 1309.1421 | (91) | 3776.1301 |
| (30) | 676.4845 | (61) | 1330.8147 | (92) | 3796.4219 |
| (31) | 687.6814 | (62) | 1339.6496 | (93) | 3835.416 |

| *Anti*-N7 at ground state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 27.3231 | (32) | 690.875 | (63) | 1353.3291 |
| (2) | 40.5575 | (33) | 739.9367 | (64) | 1360.9024 |
| (3) | 66.2368 | (34) | 764.2398 | (65) | 1368.1667 |
| (4) | 99.6611 | (35) | 793.0917 | (66) | 1373.1264 |
| (5) | 105.2984 | (36) | 846.1183 | (67) | 1395.4217 |
| (6) | 129.9643 | (37) | 864.4588 | (68) | 1408.2728 |
| (7) | 158.2119 | (38) | 902.7519 | (69) | 1417.1469 |
| (8) | 190.9691 | (39) | 906.8872 | (70) | 1427.5094 |
| (9) | 204.7029 | (40) | 914.9891 | (71) | 1442.9648 |
| (10) | 216.5486 | (41) | 924.5617 | (72) | 1451.4579 |
| (11) | 243.7927 | (42) | 981.855 | (73) | 1500.0008 |
| (12) | 258.5074 | (43) | 989.4661 | (74) | 1500.3925 |
| (13) | 268.0028 | (44) | 1000.7177 | (75) | 1528.0675 |
| (14) | 283.6208 | (45) | 1049.3396 | (76) | 1572.9584 |
| (15) | 301.3791 | (46) | 1050.7581 | (77) | 1615.4641 |
| (16) | 323.5611 | (47) | 1071.2486 | (78) | 1638.6758 |
| (17) | 330.9777 | (48) | 1094.506 | (79) | 1670.7109 |
| (18) | 358.8611 | (49) | 1108.1967 | (80) | 3013.6893 |
| (19) | 374.978 | (50) | 1116.8579 | (81) | 3054.9844 |
| (20) | 411.3596 | (51) | 1129.4781 | (82) | 3057.9966 |
| (21) | 514.26 | (52) | 1146.5785 | (83) | 3061.7815 |
| (22) | 526.4959 | (53) | 1207.5736 | (84) | 3077.4809 |
| (23) | 538.3648 | (54) | 1219.7035 | (85) | 3095.7684 |
| (24) | 555.2108 | (55) | 1226.8058 | (86) | 3187.3888 |
| (25) | 566.8096 | (56) | 1243.5575 | (87) | 3302.8568 |
| (26) | 584.4371 | (57) | 1261.2205 | (88) | 3583.7553 |
| (27) | 588.5033 | (58) | 1278.9187 | (89) | 3592.2552 |
| (28) | 619.471 | (59) | 1289.1649 | (90) | 3620.1375 |
| (29) | 649.6966 | (60) | 1302.1779 | (91) | 3717.2898 |
| (30) | 660.386 | (61) | 1331.5353 | (92) | 3762.426 |
| (31) | 682.0084 | (62) | 1335.271 | (93) | 3834.5338 |

**Table S5.** Vibration frequency of DFT optimized adenosine and conformers at excited state ($S_1$) by 6-311G++ (d,p) basis set.

| *Syn*-N1 at excited state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 37.2341 | (32) | 654.7117 | (63) | 1321.0311 |
| (2) | 48.6023 | (33) | 696.3387 | (64) | 1342.049 |
| (3) | 74.9484 | (34) | 732.2989 | (65) | 1352.9072 |
| (4) | 93.4934 | (35) | 739.8678 | (66) | 1357.0079 |
| (5) | 123.3764 | (36) | 753.2494 | (67) | 1358.4668 |
| (6) | 135.0764 | (37) | 797.6893 | (68) | 1385.2847 |
| (7) | 146.3998 | (38) | 846.8953 | (69) | 1405.42 |
| (8) | 176.6865 | (39) | 860.3638 | (70) | 1415.0784 |
| (9) | 185.0136 | (40) | 874.2938 | (71) | 1421.1096 |
| (10) | 205.4572 | (41) | 898.7294 | (72) | 1430.6551 |
| (11) | 238.4677 | (42) | 913.6922 | (73) | 1441.6494 |
| (12) | 239.8628 | (43) | 966.8042 | (74) | 1463.1594 |
| (13) | 248.2598 | (44) | 983.7747 | (75) | 1480.8103 |
| (14) | 265.6063 | (45) | 1018.8158 | (76) | 1517.8402 |
| (15) | 306.8401 | (46) | 1041.2881 | (77) | 1581.0172 |
| (16) | 327.1837 | (47) | 1049.9312 | (78) | 1654.3322 |
| (17) | 335.3291 | (48) | 1070.041 | (79) | 1669.2874 |
| (18) | 381.5186 | (49) | 1089.1044 | (80) | 3020.6423 |
| (19) | 409.2084 | (50) | 1108.0668 | (81) | 3047.702 |
| (20) | 417.2774 | (51) | 1118.4357 | (82) | 3055.7722 |
| (21) | 442.6738 | (52) | 1126.5985 | (83) | 3067.1202 |
| (22) | 484.4073 | (53) | 1153.6058 | (84) | 3083.6206 |
| (23) | 504.2339 | (54) | 1196.4577 | (85) | 3098.7507 |
| (24) | 534.5998 | (55) | 1207.0449 | (86) | 3253.2397 |
| (25) | 536.3482 | (56) | 1222.9885 | (87) | 3264.7159 |
| (26) | 547.8979 | (57) | 1237.5506 | (88) | 3541.6025 |
| (27) | 573.9558 | (58) | 1256.3442 | (89) | 3561.5933 |
| (28) | 596.1758 | (59) | 1269.7705 | (90) | 3575.3232 |
| (29) | 608.0325 | (60) | 1294.2535 | (91) | 3658.4752 |
| (30) | 631.5527 | (61) | 1310.4652 | (92) | 3749.5818 |
| (31) | 636.6272 | (62) | 1316.4543 | (93) | 3832.8963 |

| *Syn*-N3 at excited state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 37.77 | (32) | 683.6926 | (63) | 1311.8347 |
| (2) | 43.1395 | (33) | 716.5159 | (64) | 1343.4479 |
| (3) | 71.127 | (34) | 721.2298 | (65) | 1350.3326 |
| (4) | 88.271 | (35) | 733.1048 | (66) | 1354.0453 |
| (5) | 113.2537 | (36) | 737.8575 | (67) | 1377.4333 |
| (6) | 125.2531 | (37) | 765.2733 | (68) | 1382.0773 |
| (7) | 150.7891 | (38) | 808.6525 | (69) | 1408.8446 |
| (8) | 155.9766 | (39) | 846.669 | (70) | 1425.4963 |
| (9) | 207.1861 | (40) | 870.378 | (71) | 1435.9659 |
| (10) | 217.7444 | (41) | 898.0795 | (72) | 1441.5231 |
| (11) | 225.4541 | (42) | 919.6711 | (73) | 1445.2208 |
| (12) | 244.7496 | (43) | 936.2577 | (74) | 1486.4097 |
| (13) | 270.696 | (44) | 978.636 | (75) | 1498.5407 |
| (14) | 274.8104 | (45) | 992.6553 | (76) | 1519.2069 |
| (15) | 278.7553 | (46) | 1042.0121 | (77) | 1559.6794 |
| (16) | 319.037 | (47) | 1054.2424 | (78) | 1616.9333 |
| (17) | 322.8857 | (48) | 1065.9505 | (79) | 1644.1768 |
| (18) | 354.0212 | (49) | 1074.6445 | (80) | 3038.1326 |
| (19) | 372.4432 | (50) | 1087.7964 | (81) | 3051.4121 |
| (20) | 418.4344 | (51) | 1113.7429 | (82) | 3075.7148 |
| (21) | 426.8267 | (52) | 1115.9732 | (83) | 3086.3557 |
| (22) | 448.9332 | (53) | 1129.3642 | (84) | 3095.0209 |
| (23) | 458.4557 | (54) | 1199.5188 | (85) | 3102.5077 |
| (24) | 488.5233 | (55) | 1215.8153 | (86) | 3173.0118 |
| (25) | 492.6099 | (56) | 1221.3077 | (87) | 3265.2777 |
| (26) | 509.9431 | (57) | 1237.0744 | (88) | 3268.8159 |
| (27) | 531.5711 | (58) | 1264.1974 | (89) | 3546.5132 |
| (28) | 542.3991 | (59) | 1271.7488 | (90) | 3672.5502 |
| (29) | 587.7754 | (60) | 1280.1725 | (91) | 3718.5155 |
| (30) | 614.2411 | (61) | 1285.3172 | (92) | 3823.4718 |
| (31) | 629.6048 | (62) | 1291.6918 | (93) | 3838.1772 |

| *Syn*-N7 at excited state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 37.77 | (32) | 683.6926 | (63) | 1311.8347 |
| (2) | 43.1395 | (33) | 716.5159 | (64) | 1343.4479 |
| (3) | 71.127 | (34) | 721.2298 | (65) | 1350.3326 |
| (4) | 88.271 | (35) | 733.1048 | (66) | 1354.0453 |
| (5) | 113.2537 | (36) | 737.8575 | (67) | 1377.4333 |
| (6) | 125.2531 | (37) | 765.2733 | (68) | 1382.0773 |
| (7) | 150.7891 | (38) | 808.6525 | (69) | 1408.8446 |
| (8) | 155.9766 | (39) | 846.669 | (70) | 1425.4963 |
| (9) | 207.1861 | (40) | 870.378 | (71) | 1435.9659 |
| (10) | 217.7444 | (41) | 898.0795 | (72) | 1441.5231 |
| (11) | 225.4541 | (42) | 919.6711 | (73) | 1445.2208 |
| (12) | 244.7496 | (43) | 936.2577 | (74) | 1486.4097 |
| (13) | 270.696 | (44) | 978.636 | (75) | 1498.5407 |
| (14) | 274.8104 | (45) | 992.6553 | (76) | 1519.2069 |
| (15) | 278.7553 | (46) | 1042.0121 | (77) | 1559.6794 |
| (16) | 319.037 | (47) | 1054.2424 | (78) | 1616.9333 |
| (17) | 322.8857 | (48) | 1065.9505 | (79) | 1644.1768 |
| (18) | 354.0212 | (49) | 1074.6445 | (80) | 3038.1326 |
| (19) | 372.4432 | (50) | 1087.7964 | (81) | 3051.4121 |
| (20) | 418.4344 | (51) | 1113.7429 | (82) | 3075.7148 |
| (21) | 426.8267 | (52) | 1115.9732 | (83) | 3086.3557 |
| (22) | 448.9332 | (53) | 1129.3642 | (84) | 3095.0209 |
| (23) | 458.4557 | (54) | 1199.5188 | (85) | 3102.5077 |
| (24) | 488.5233 | (55) | 1215.8153 | (86) | 3173.0118 |
| (25) | 492.6099 | (56) | 1221.3077 | (87) | 3265.2777 |
| (26) | 509.9431 | (57) | 1237.0744 | (88) | 3268.8159 |
| (27) | 531.5711 | (58) | 1264.1974 | (89) | 3546.5132 |
| (28) | 542.3991 | (59) | 1271.7488 | (90) | 3672.5502 |
| (29) | 587.7754 | (60) | 1280.1725 | (91) | 3718.5155 |
| (30) | 614.2411 | (61) | 1285.3172 | (92) | 3823.4718 |
| (31) | 629.6048 | (62) | 1291.6918 | (93) | 3838.1772 |

| *Anti*-N1 at excited state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 27.4936 | (32) | 657.2573 | (63) | 1318.0081 |
| (2) | 45.745 | (33) | 681.4587 | (64) | 1342.7949 |
| (3) | 58.4868 | (34) | 734.4316 | (65) | 1346.1161 |
| (4) | 92.3482 | (35) | 747.0408 | (66) | 1350.8111 |
| (5) | 99.6681 | (36) | 759.7964 | (67) | 1364.0706 |
| (6) | 110.1019 | (37) | 783.8936 | (68) | 1378.1236 |
| (7) | 127.8236 | (38) | 833.2099 | (69) | 1421.9759 |
| (8) | 135.6152 | (39) | 865.269 | (70) | 1426.6704 |
| (9) | 172.3361 | (40) | 889.3896 | (71) | 1433.9504 |
| (10) | 194.1626 | (41) | 922.5835 | (72) | 1445.028 |
| (11) | 224.8388 | (42) | 924.5301 | (73) | 1448.3757 |
| (12) | 233.2861 | (43) | 971.0053 | (74) | 1474.8538 |
| (13) | 244.5635 | (44) | 977.9774 | (75) | 1499.1768 |
| (14) | 252.0315 | (45) | 1020.9742 | (76) | 1522.8524 |
| (15) | 266.3035 | (46) | 1041.0429 | (77) | 1574.0516 |
| (16) | 301.4507 | (47) | 1055.9494 | (78) | 1652.6748 |
| (17) | 319.519 | (48) | 1078.797 | (79) | 1674.8384 |
| (18) | 334.3694 | (49) | 1089.908 | (80) | 3016.4662 |
| (19) | 349.7495 | (50) | 1110.0519 | (81) | 3057.731 |
| (20) | 393.3865 | (51) | 1115.2918 | (82) | 3065.3391 |
| (21) | 421.3267 | (52) | 1131.4633 | (83) | 3075.7226 |
| (22) | 444.7495 | (53) | 1135.4459 | (84) | 3089.4832 |
| (23) | 461.0058 | (54) | 1196.8121 | (85) | 3115.8271 |
| (24) | 477.8687 | (55) | 1201.1347 | (86) | 3229.6703 |
| (25) | 521.9864 | (56) | 1208.4473 | (87) | 3254.3356 |
| (26) | 538.8598 | (57) | 1218.038 | (88) | 3542.9492 |
| (27) | 571.7486 | (58) | 1242.8146 | (89) | 3581.0627 |
| (28) | 581.7666 | (59) | 1262.3467 | (90) | 3657.8998 |
| (29) | 600.5631 | (60) | 1271.7767 | (91) | 3729.3896 |
| (30) | 612.0304 | (61) | 1295.5355 | (92) | 3832.7215 |
| (31) | 635.721 | (62) | 1310.3533 | (93) | 3838.59 |

| *Anti*-N3 at excited state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 20.1314 | (32) | 632.9824 | (63) | 1326.4344 |
| (2) | 30.7878 | (33) | 672.1492 | (64) | 1332.4354 |
| (3) | 56.0401 | (34) | 721.0082 | (65) | 1343.3756 |
| (4) | 76.1124 | (35) | 724.8937 | (66) | 1358.0045 |
| (5) | 97.48 | (36) | 752.4389 | (67) | 1363.8963 |
| (6) | 110.984 | (37) | 760.406 | (68) | 1377.249 |
| (7) | 128.9198 | (38) | 818.1341 | (69) | 1398.1651 |
| (8) | 175.4196 | (39) | 835.6623 | (70) | 1416.4155 |
| (9) | 176.2414 | (40) | 863.3385 | (71) | 1436.4932 |
| (10) | 203.5416 | (41) | 899.4618 | (72) | 1445.5753 |
| (11) | 210.3581 | (42) | 916.3001 | (73) | 1450.4085 |
| (12) | 217.9472 | (43) | 928.6757 | (74) | 1454.7479 |
| (13) | 252.3629 | (44) | 980.5878 | (75) | 1498.6867 |
| (14) | 262.6309 | (45) | 1004.0443 | (76) | 1510.0056 |
| (15) | 272.599 | (46) | 1036.4348 | (77) | 1541.8477 |
| (16) | 301.925 | (47) | 1052.746 | (78) | 1611.2677 |
| (17) | 325.6027 | (48) | 1067.2807 | (79) | 1637.5854 |
| (18) | 344.7384 | (49) | 1080.8693 | (80) | 3013.8423 |
| (19) | 359.2413 | (50) | 1084.816 | (81) | 3023.625 |
| (20) | 397.8883 | (51) | 1105.2567 | (82) | 3056.8695 |
| (21) | 407.4235 | (52) | 1117.1751 | (83) | 3060.4371 |
| (22) | 428.3239 | (53) | 1135.4261 | (84) | 3089.8309 |
| (23) | 458.2181 | (54) | 1195.2696 | (85) | 3101.0478 |
| (24) | 482.8581 | (55) | 1205.6387 | (86) | 3267.121 |
| (25) | 486.0973 | (56) | 1215.2242 | (87) | 3294.8547 |
| (26) | 511.7973 | (57) | 1245.1978 | (88) | 3469.895 |
| (27) | 539.581 | (58) | 1252.6323 | (89) | 3548.479 |
| (28) | 550.0195 | (59) | 1266.9823 | (90) | 3674.3239 |
| (29) | 566.1273 | (60) | 1277.4235 | (91) | 3770.5356 |
| (30) | 598.6623 | (61) | 1289.2345 | (92) | 3800.8911 |
| (31) | 612.5885 | (62) | 1306.7067 | (93) | 3836.1867 |

| *Anti*-N7 at excited state | | | | | |
|---|---|---|---|---|---|
| Order | Value | Order | Value | Order | Value |
| (1) | 9.1604 | (32) | 649.563 | (63) | 1342.2208 |
| (2) | 38.854 | (33) | 675.3222 | (64) | 1354.3466 |
| (3) | 72.0213 | (34) | 728.8907 | (65) | 1359.4698 |
| (4) | 80.5797 | (35) | 748.4502 | (66) | 1364.8752 |
| (5) | 114.2052 | (36) | 756.7987 | (67) | 1374.7602 |
| (6) | 131.477 | (37) | 831.8657 | (68) | 1392.5133 |
| (7) | 136.1417 | (38) | 862.1683 | (69) | 1406.0858 |
| (8) | 162.5848 | (39) | 881.9097 | (70) | 1419.08 |
| (9) | 188.7409 | (40) | 900.296 | (71) | 1423.8504 |
| (10) | 204.3591 | (41) | 923.4024 | (72) | 1433.7078 |
| (11) | 207.7745 | (42) | 949.0318 | (73) | 1444.699 |
| (12) | 233.4388 | (43) | 983.7324 | (74) | 1449.2064 |
| (13) | 239.4179 | (44) | 986.145 | (75) | 1491.3949 |
| (14) | 254.4933 | (45) | 1029.8634 | (76) | 1497.9521 |
| (15) | 289.4226 | (46) | 1047.7272 | (77) | 1551.2908 |
| (16) | 296.1423 | (47) | 1063.5079 | (78) | 1566.855 |
| (17) | 334.4353 | (48) | 1078.2886 | (79) | 1651.646 |
| (18) | 351.6223 | (49) | 1087.86 | (80) | 2997.5035 |
| (19) | 372.131 | (50) | 1090.9116 | (81) | 3010.564 |
| (20) | 392.0454 | (51) | 1109.9733 | (82) | 3052.8582 |
| (21) | 413.8929 | (52) | 1117.8486 | (83) | 3057.3985 |
| (22) | 428.596 | (53) | 1126.0689 | (84) | 3075.4413 |
| (23) | 489.0358 | (54) | 1193.9362 | (85) | 3084.3366 |
| (24) | 512.2667 | (55) | 1206.1047 | (86) | 3211.573 |
| (25) | 520.7431 | (56) | 1224.2372 | (87) | 3252.0113 |
| (26) | 527.4787 | (57) | 1244.8203 | (88) | 3540.1862 |
| (27) | 544.9779 | (58) | 1259.1969 | (89) | 3571.3761 |
| (28) | 573.541 | (59) | 1268.4531 | (90) | 3663.2692 |
| (29) | 590.8953 | (60) | 1282.8086 | (91) | 3666.8274 |
| (30) | 634.4896 | (61) | 1298.5662 | (92) | 3766.9466 |
| (31) | 648.1087 | (62) | 1333.5545 | (93) | 3834.8035 |

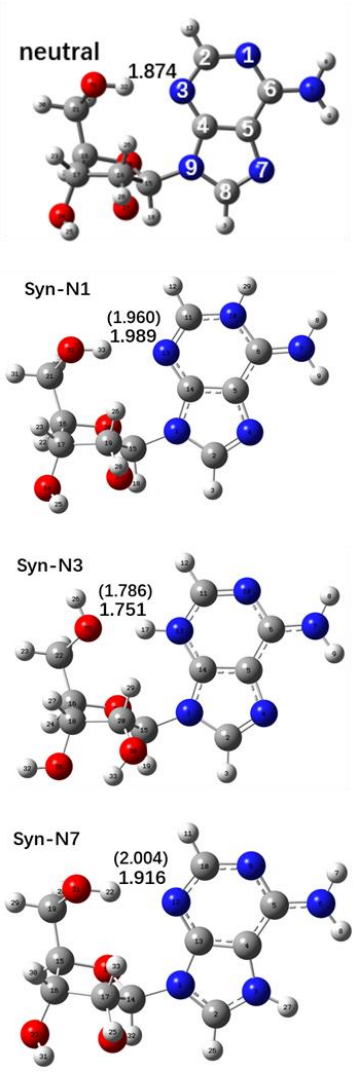


**Fig. S2** Optimized structures calculated for Ado in neutral form and with protonation occurring at the N1, N3 and N7 position at the *syn*-conformations. Values with and without bracket represent the bond lengths of the conformers obtained at the lowest energy excited state and the ground state, respectively.

**Table S6** Gibbs free energy of protonated adenosine of different tautomeric forms at the ground and excited states from theoretical calculation under the bulk solvent condition.

| | | *syn*-N1 | *syn*-N3 | *syn*-N7 | a*nti*-N1 | *anti*-N3 | *anti*-N7 |
|---|---|---|---|---|---|---|---|
| $S_0$ | ΔG /Hartree | -964.069 | -964.072 | -964.064 | -964.068 | -964.065 | -964.064 |
| $S_1$ | ΔG /Hartree | -963.919 | -963.921 | -963.920 | -963.918 | -963.917 | -963.915 |

**Table S7** Thermodynamics parameters, calculated absorption and emission energies of protonated adenosine of different tautomeric forms at the ground and excited state from theoretical calculation under the inclusion of two water molecules (-2W) and in the gas phase (gas).

| | | *syn*-N1-2W | *syn*-N3-2W | *syn*-N1-gas | *syn*-N3-gas |
|---|---|---|---|---|---|
| $S_0$ | $E_{ToT}$ /Hartree [a] | -1117.247 | -1117.242 | -964.197 | -964.214 |
| | ΔG /Hartree [b] | -1116.985 | -1116.981 | -963.976 | -963.993 |
| | $\lambda_a$ /nm [c] (eV) [d] | 250 (4.97) | 261 (3.88) | 256 (4.84) | 255 (4.87) |
| | f [e] | 0.096 | 0.286 | 0.106 | 0.176 |
| | Transition orbitals [f] | H-1→L (46%) | H→L (83%) | H-3→L (68%) | H→L (58%) |
| $S_1$ | $E_{ToT}$ /Hartree [a] | -1117.091 | -1117.085 | -964.133 | -964.071 |
| | ΔG /Hartree [b] | -1116.835 | -1116.831 | -963.919 | -963.859 |
| | $\lambda_f$ /nm [g] (eV) [h] | 404 (3.07) | 320 (3.07) | 412 (3.01) | 298 (4.16) |
| | f [i] | 0.123 | 0.389 | 0.120 | 0.205 |
| | Transition orbitals [f] | H←L (97%) | H←L (97%) | H←L (96%) | H-1←L (94%) |

[a] Single point energy; [b] Gibbs free energy; [c] Calculated absorption energy in wavelength, [d] electron volt and [e] oscillator strength at the maximum absorption; [f] Molecular orbital of the corresponding electronic transition with H denoting for HOMO, L for LUMO and the bracketed value for percentage contribution of the correlated transition; [g] Calculated fluorescence emission energy in wavelength, [h] electron volt and [i] oscillator strength at the maximum fluorescence intensity.

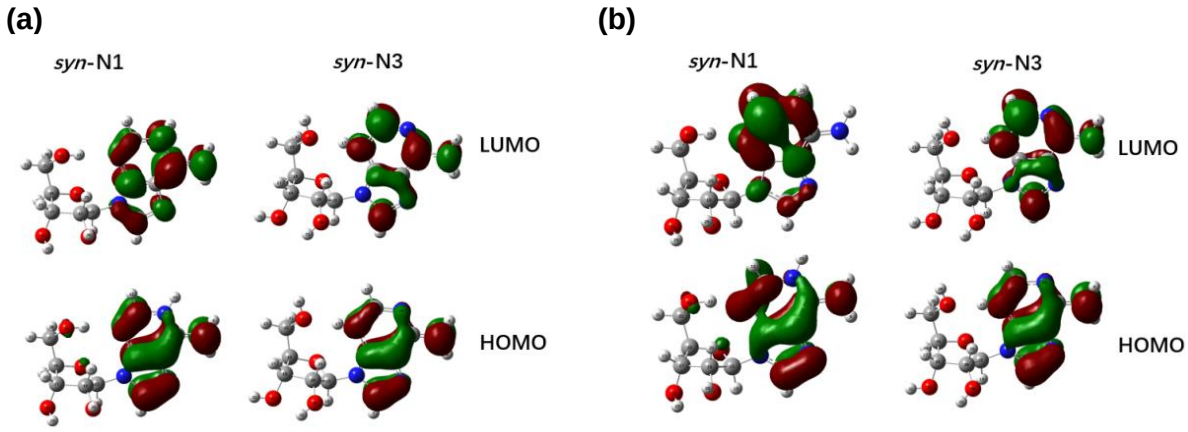


**Fig. S3** Molecular orbitals of *syn*-N1 and *syn*-N3 involved in the transition of (a) electronic absorption and (b) fluorescence.

**Table S8** Structural parameters for the optimized structures of protonated adenosine of different tautomeric forms at the ground and excited state from the theoretical calculation under the bulk solvent condition.

| | *syn*-N1 | *syn*-N3 | *syn*-N7 | *anti*-N1 | *anti*-N3 | *anti*-N7 |
|---|---|---|---|---|---|---|
| N1-C2 /Å | 1.37(1.39) | 1.31(1.33) | 1.33(1.31) | 1.37(1.40) | 1.31(1.33) | 1.33(1.31) |
| N3-C2 /Å | 1.30(1.39) | 1.35(1.45) | 1.34(1.37) | 1.30(1.39) | 1.35(1.45) | 1.34(1.37) |
| N3-C4 /Å | 1.35(1.30) | 1.36(1.33) | 1.33(1.32) | 1.35(1.30) | 1.36(1.33) | 1.33(1.32) |
| C4-C5 /Å | 1.40(1.45) | 1.39(1.42) | 1.39(1.40) | 1.40(1.45) | 1.39(1.42) | 1.39(1.41) |
| C5-C6 /Å | 1.41(1.42) | 1.41(1.47) | 1.42(1.40) | 1.41(1.42) | 1.41(1.47) | 1.42(1.41) |
| N1-C6 /Å | 1.37(1.37) | 1.36(1.33) | 1.35(1.37) | 1.37(1.38) | 1.36(1.33) | 1.35(1.37) |
| N9-C4 /Å | 1.37(1.38) | 1.36(1.37) | 1.40(1.38) | 1.37(1.38) | 1.36(1.37) | 1.39(1.38) |
| N9-C8 /Å | 1.38(1.38) | 1.39(1.38) | 1.34(1.40) | 1.38(1.38) | 1.39(1.37) | 1.34(1.39) |
| N7-C8 /Å | 1.31(1.32) | 1.31(1.35) | 1.33(1.42) | 1.31(1.32) | 1.31(1.35) | 1.33(1.42) |
| N7-C5 /Å | 1.37(1.36) | 1.38(1.34) | 1.39(1.38) | 1.37(1.36) | 1.38(1.34) | 1.39(1.38) |
| Nexo-C6 /Å | 1.32(1.32) | 1.33(1.34) | 1.34(1.34) | 1.33(1.32) | 1.33(1.34) | 1.34(1.34) |
| C5-C6-N1 /° | 113.80(116.01) | 118.70(119.90) | 116.64(119.87) | 113.81(115.98) | 118.78(119.70) | 116.68(119.83) |
| N1-C2-N3 /° | 124.27(117.85) | 125.41(123.31) | 127.96(126.61) | 124.39(117.12) | 124.87(123.02) | 127.75(126.42) |
| C5-C4-N3 /° | 126.01(123.43) | 121.81(122.43) | 125.37(123.84) | 126.73(122.90) | 121.91(122.82) | 126.34(124.28) |
| C4-C5-N7 /° | 111.36(109.99) | 110.22(110.92) | 106.57(108.79) | 111.11(109.89) | 109.86(110.50) | 106.16(108.18) |
| N7-C8-N9 /° | 113.68(113.77) | 113.48(112.39) | 110.16(108.22) | 113.27(113.53) | 113.22(112.03) | 109.70(107.65) |
| C8-N9-C4 /° | 105.88(106.19) | 105.24(105.95) | 107.86(107.88) | 106.18(106.43) | 105.23(106.12) | 108.27(107.72) |
| C5-C4-N3-C2 /° | -0.44(-13.28) | -0.41(-0.94) | -0.24(-1.67) | 0.26(-14.57) | -0.27(0.097) | -0.59(1.95) |
| C4-N9-C1'-H /° | 174.82(-179.73) | 168.72(171.27) | 175.34(176.32) | -2.89(-0.71) | -60.63(-55.16) | -64.46(-69.02) |
| N7-C5-C4-N3 /° | -179.47(-169.17) | -179.28(-179.22) | 179.89(-176.88) | 179.48(-169.63) | -179.66(-178.96) | -178.78(-179.43) |
| C8-N9-C4-N3 /° | 179.25(170.31) | 178.99(178.93) | 179.83(176.12) | -179.45(170.79) | 179.84(179.43) | 178.84(-173.54) |
| C5-C4-N9-C8 /° | -0.42(0.33) | -0.28(-0.51) | -0.26(-3.56) | 0.49(1.88) | 0.34(0.34) | -0.13(6.10) |
| C2'-C1'-N9-C4 /° | -64.63(-58.82) | -69.34(-66.99) | -64.36(-63.26) | 118.66(120.83) | 61.40(66.32) | 56.86(53.82) |
| Nexo-C6-C5-C4 /° | 179.57(-164.80) | -179.95(179.90) | -179.36(179.93) | -179.71(-167.73) | 179.98(-179.69) | 179.45(-177.67) |

Values with and without bracket represent parameters from the optimized structures at the excited state and ground state, respectively.

**Table S9** Structural parameters for the optimized structures of protonated adenosine of different tautomeric forms at the ground and excited state from the theoretical calculation under the inclusion of two water molecules (-2W) and in the gas phase (gas).

| | *syn*-N1-2w | *syn*-N1-gas | *syn*-N3-2w | *syn*-N3-2w-gas |
|---|---|---|---|---|
| N1-C2 /Å | 1.36(1.39) | 1.38(1.39) | 1.31(1.34) | 1.30(1.32) |
| N3-C2 /Å | 1.30(1.40) | 1.30(1.39) | 1.35(1.44) | 1.36(1.45) |
| N3-C4 /Å | 1.35(1.30) | 1.35(1.30) | 1.36(1.32) | 1.36(1.38) |
| C4-C5 /Å | 1.39(1.45) | 1.40(1.45) | 1.39(1.43) | 1.39(1.35) |
| C5-C6 /Å | 1.41(1.42) | 1.40(1.42) | 1.42(1.46) | 1.41(1.46) |
| N1-C6 /Å | 1.37(1.38) | 1.37(1.37) | 1.37(1.33) | 1.36(1.32) |
| N9-C4 /Å | 1.37(1.39) | 1.37(1.38) | 1.37(1.37) | 1.36(1.41) |
| N9-C8 /Å | 1.38(1.38) | 1.38(1.38) | 1.38(1.38) | 1.39(1.41) |
| N7-C8 /Å | 1.37(1.32) | 1.31(1.32) | 1.31(1.34) | 1.30(1.29) |
| N7-C5 /Å | 1.38(1.37) | 1.37(1.36) | 1.38(1.34) | 1.37(1.39) |
| Nexo-C6 /Å | 1.31(1.32) | 1.33(1.32) | 1.32(1.34) | 1.33(1.36) |
| | | | | |
| C5-C6-N1 /° | 113.54(115.83) | 114.08(116.01) | 117.60(119.61) | 118.76(117.92) |
| N1-C2-N3 /° | 124.49(118.31) | 124.20(117.86) | 125.26(122.71) | 125.46(124.16) |
| C5-C4-N3 /° | 126.30(124.29) | 125.42(123.44) | 122.05(122.50) | 121.67(125.35) |
| C4-C5-N7 /° | 110.73(109.70) | 111.62(109.98) | 109.63(110.20) | 110.40(111.16) |
| N7-C8-N9 /° | 113.35(113.79) | 113.94(113.77) | 113.11(112.39) | 113.43(111.70) |
| C8-N9-C4 /° | 106.08(106.36) | 105.80(106.19) | 105.45(105.96) | 105.14(105.47) |
| | | | | |
| C5-C4-N3-C2 /° | -0.29(-12.15) | 0.43(-13.28) | -0.35(-1.57) | -0.12(1.51) |
| C4-N9-C1'-H /° | 175.10(-179.74) | 169.72(-179.67) | 168.29(170.40) | 166.05(-176.76) |
| N7-C5-C4-N3 /° | -179.57(-171.15) | 179.91(-169.15) | -179.50(-179.16) | -179.45(172.25) |
| C8-N9-C4-N3 /° | 179.34(172.18) | 179.90(170.29) | 179.21(178.95) | 179.25(-171.56) |
| C5-C4-N9-C8 /° | -0.39(0.55) | -0.19(0.32) | -0.21(-0.34) | -0.07(-1.03) |
| C2'-C1'-N9-C4 /° | -64.32(-58.92) | -70.28(-58.76) | -69.80(-67.85) | -71.81(-64.71) |
| Nexo-C6-C5-C4 /° | -179.93(-166.55) | -179.48(-164.80) | 179.96(-178.98) | -179.89(-174.20) |

Values with and without bracket represent parameters from the optimized structures at the excited state and ground state, respectively.

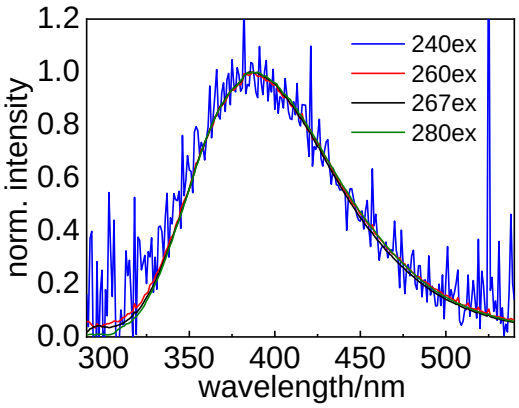


**Fig. S4** Fluorescence spectra from Ado recorded in buffer solution at pH3 condition under excitation at wavelengths of 240 nm (blue), 260 nm (red), 267 nm (black) and 280 nm (green).

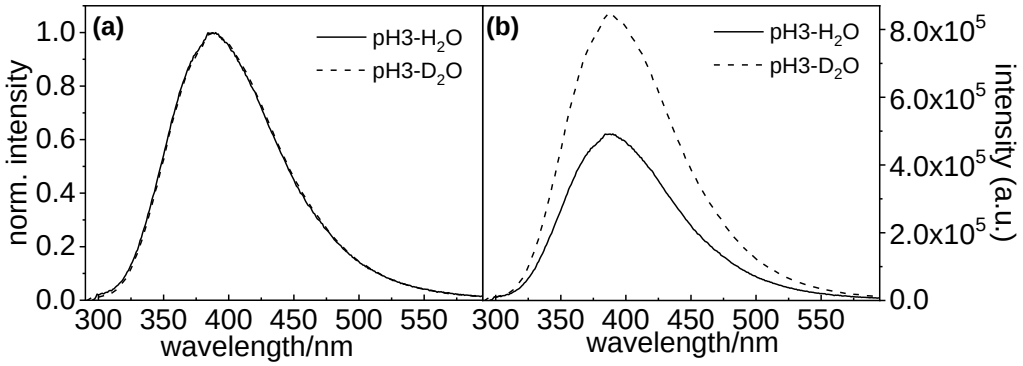


**Fig. S5** Fluorescence spectra from Ado recorded in pH3 $H_2O$ (solid line) and $D_2O$ (dashed line) buffer at (a) the normalized and (b) relative intensity scale.

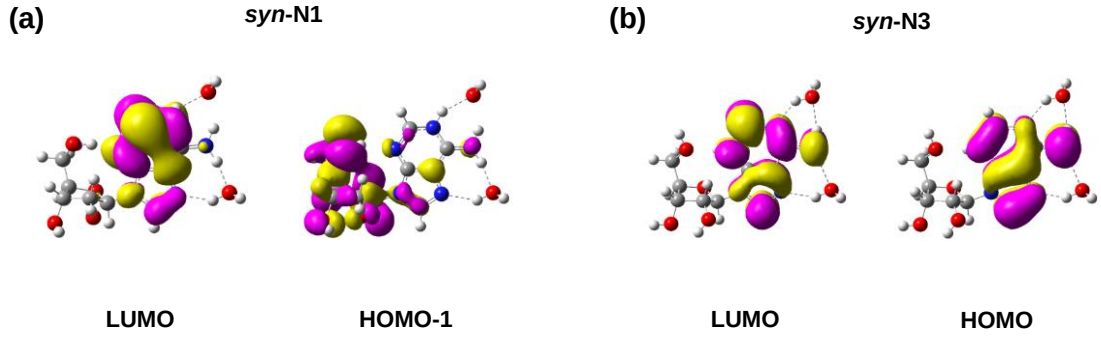


**Fig. S6** Molecular orbitals of (a) *syn*-N1 and (b) *syn*-N3 involved in the transition of electronic fluorescence with the inclusion of two water molecules.

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