Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Tracking the origin of photostability in purine nucleobases: the photophysics of 2-oxopurine

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Figure S1. Molecular orbitals involved in the (14,11) active space used for the CASSCF calculations.

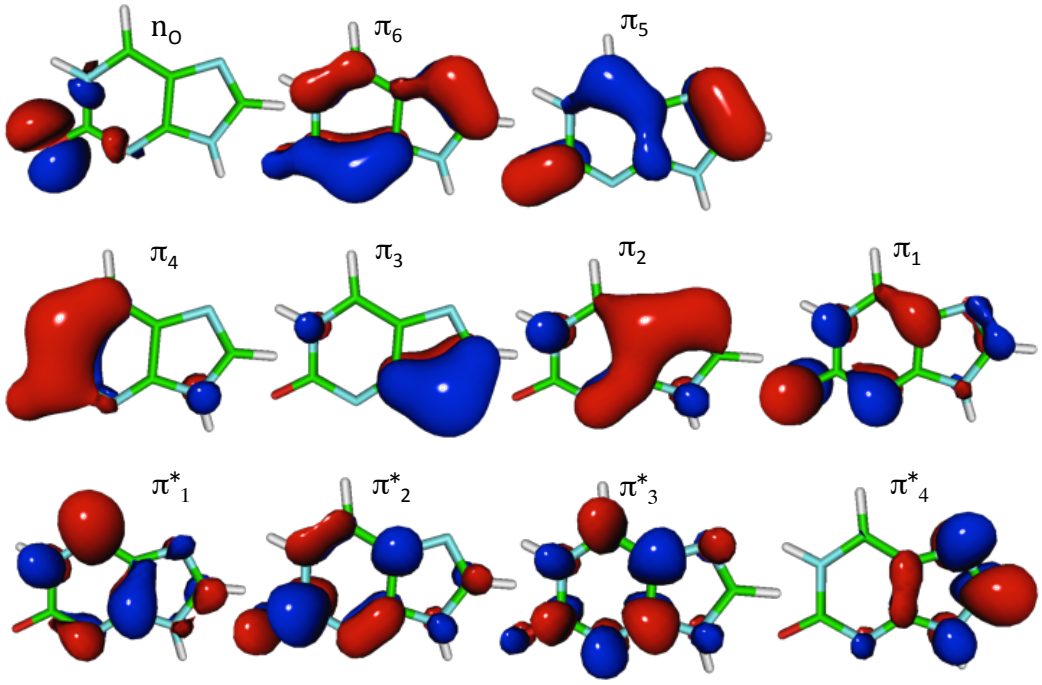

Figure S2. 2-oxopurine gas phase simulated absorption spectra computed at the (a) MS(14)-CASPT2 (black), ADC(2) (red) and CC2 (blue) levels of theory and (b) TD-M062X level of theory in gas phase (solid green) and water (dashed green) in the range comprised between 180-400 nm. A total number of $^{CASPT2}13$, $^{ADC2}10$, $^{CC2}10$ and $^{TD\text{-}M062X}10$ excited states have been considered in the simulations.

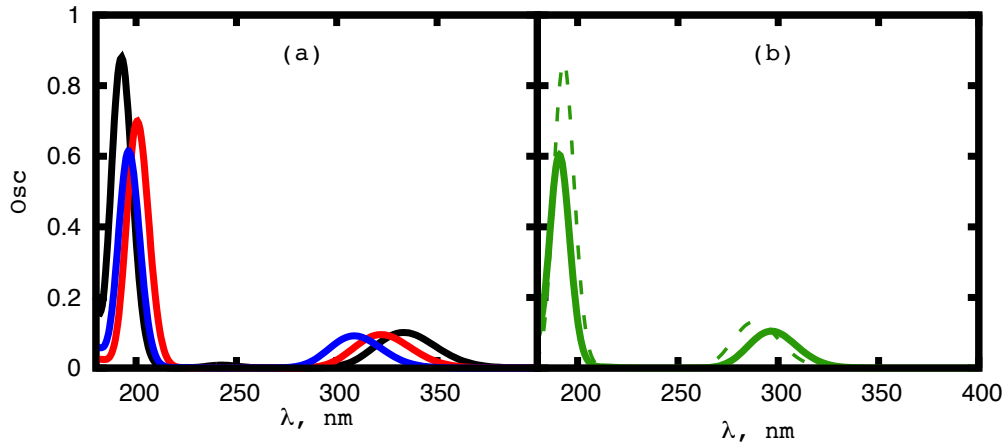

Figure S3. Density difference (S_n-S_0) computed with the perturbatively modified CASSCF wave functions.

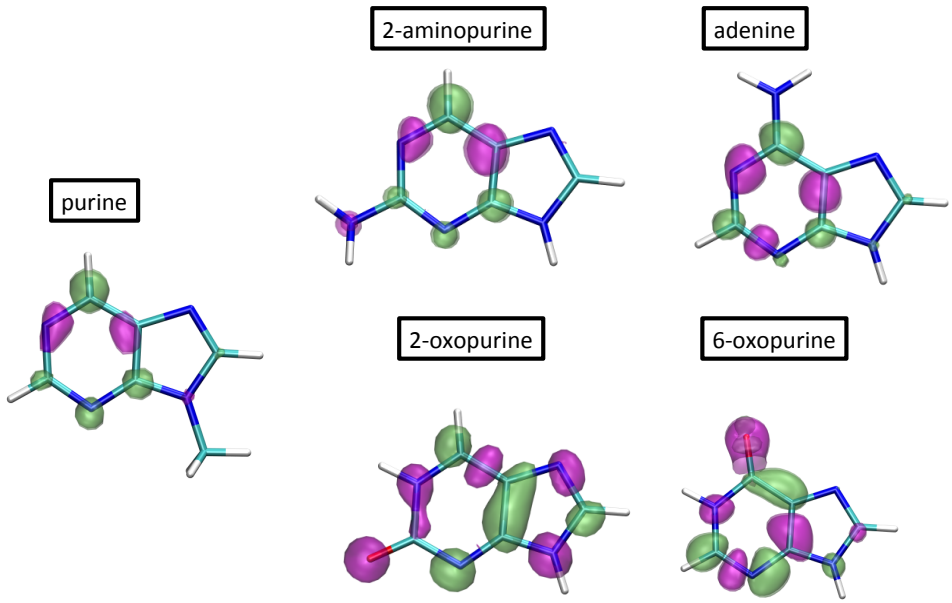

Figure S4. 2-oxopurine S_1 potential energy profile evaluated at the M062X/PCM-M062X level of theory considering different solvents, i.e acetonitrile (ACN), toluene (TOL). Gas phase (GP) energies and water state specific equilibrium (EQ) and non-equilibrium (NEQ) energies relative to the S_0 are also included for comparison.

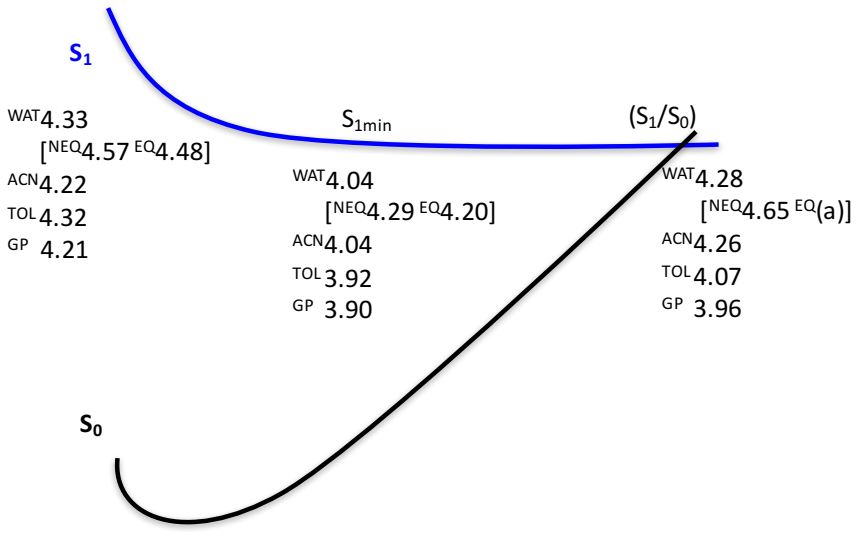

Figure S5. CASSCF Minimum Energy Paths connecting the Franck Condon and S_{1min} regions (left panel) and the S_1/S_0 crossing with the S_{1min} (right panel) along the S_1 potential energy surface.

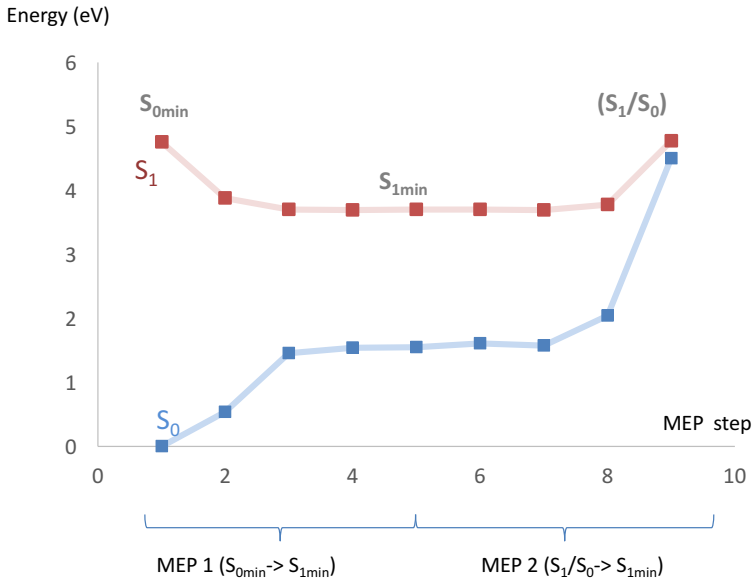

Table S1. Main configurations and their weights, energies (in nm and eV), oscillator strengths and dipole moments of the lowest lying singlet excited states of 2-oxopurine according to the MS-CASPT2, ADC(2), CC2 and M062X methods. * mixed character states

	Main Configurations	Weights	Energies (nm)	Energies (eV)	f	μ
	MS-CASPT2 IPEA=0.00 (0.25)/SA(5)					
S_1	$\pi_1\pi_1^*$	0.75 (0.75)	321 (300)	3.86 (4.13)	0.0903 (0.0954)	
S_2	$n_O\pi_1^*$	0.78 (0.78)	249 (239)	4.97 (5.18)	0.0004 (0.0004)	
S_3	$\pi_2\ \pi_1^*$ $\pi_1\pi_2^*$	0.44 (0.44) 0.12 (0.12)	239 (219)	5.20 (5.66)	0.0109 (0.0124)	
S_4	$n_O\pi_2^*$	0.81 (0.80)	202 (196)	6.13 (6.32)	0.0001 (0.0001)	
MS-CASPT2 IPEA=0.00/SA(14)						
S_0						4.1635
S_1	$\pi_1\pi_1^*$	0.76	331	3.75	0.1010	1.2735
S_2	$n_O\pi_1^*$	0.77	241	5.14	0.0004	2.2725
S_3	$\pi_2\ \pi_1^*$	0.52	241	5.15	0.0078	3.6992
S_4	$\pi_1\pi_2^*$	0.45	215	5.78	0.0548	0.885
S_5	$n_O\pi_2^*$	0.70	196	6.31	0.0000	2.36
S_6	$\pi_2\pi_2^*$	0.45	194	6.40	0.1120	3.4693
S_7	$\pi_1\pi_4^*$	0.40	191	6.50	0.7523	2.6099
S_8	*	*	172	7.22	0.6600	4.3261
S_9	*	*	166	7.46	0.1158	2.6862
S_{10}	*	*	154	8.04	0.0001	4.6958

S_{11}	*	*	152	8.17	0.0111	1.5872
S_{12}	*	*	145	8.57	0.3226	4.5148
S_{13}	*	*	133	9.35	0.0000	2.5609
	ADC(2)					
S_1	$\pi_1\pi_1^*$	0.89	320	3.87	0.0945	
S_2	$(n_O+n_N)\pi_1^*$	0.88	281	4.42	0.0002	
S_3	$(n_O-n_N)\pi_1^*$	0.86	257	4.82	0.0003	
S_4	$\pi_2\pi_1^*$ $\pi_1\pi_2^*$	0.65 0.25	227	5.45	0.0006	
S_5	$(n_O-n_N)\pi_3^*$ $(n_O+n_N)\pi_2^*$ $(n_O-n_N)\pi_2^*$ $(n_O+n_N)\pi_3^*$	0.26 0.26 0.20 0.19	207	5.99	0.00002	
S_6	$\pi_1\pi_2^*$ $\pi_2\pi_1^*$	0.59 0.22	199	6.23	0.6931	
S_7	$(n_{N1}+n_{N2})\pi_1^*$	0.71	199	6.23	0.0064	
S_8	π_1Ryd_1	0.81	196	6.33	0.0001	
S_9	π_1Ryd_2	0.74	183	6.78	0.0000	
S_{10}	$\pi_1\pi_3^*$ $\pi_5\pi_1^*$	0.52 0.26	180	6.87	0.0242	
	CC2					
S_1	$\pi_1\pi_1^*$	0.89	307	4.04	0.0910	
S_2	$(n_O+n_N)\pi_1^*$	0.93	272	4.56	0.0003	
S_3	$(n_O-n_N)\pi_1^*$	0.92	250	4.95	0.0003	
S_4	$\pi_2\pi_1^*$ $\pi_1\pi_2^*$	0.66 0.25	224	5.54	0.0016	
S_5	$(n_O+n_N)\pi_2^*$ $(n_O-n_N)\pi_3^*$ $(n_{N1}+n_{N2})\pi_1^*$ $(n_O+n_N)\pi_3^*$	0.40 0.17 0.17 0.13	198	6.27	0.0014	
S_6	π_1Ryd_1	0.79	196	6.31	0.0002	
S_7	$\pi_1\pi_2^*$ $\pi_2\pi_1^*$	0.62 0.21	195	6.36	0.6084	
S_8	$(n_{N1}+n_{N2})\pi_1^*$ $(n_O-n_N)\pi_2^*$	0.54 0.21	195	6.37	0.0051	
S_9	π_1Ryd_2	0.76	183	6.78	0.0001	
S_{10}	$\pi_1\pi_3^*$	0.65	178	6.96	0.0582	
	TD-M062X (PCM)					
S_1	$\pi_1\pi_1^*$ ($\pi_1\pi_1^*$)	0.49 (0.49)	294 (286)	4.21 (4.33)	0.1046 (0.1328)	
S_2	$(n_O+n_N)\pi_1^*$ ($(n_O+n_N)\pi_1^*$)	0.41 (0.45)	261 (247)	4.75 (5.02)	0.0002 (0.0002)	
S_3	$\pi_2\pi_1^*$ ($\pi_2\pi_1^*$) $\pi_1\pi_2^*$ ($\pi_1\pi_2^*$)	0.29 (0.32) 0.19 (0.16)	212 (212)	5.86 (5.84)	0.0026 (0.0004)	
S_4	$(n_O-n_N)\pi_1^*$ ($(n_O-n_N)\pi_1^*$)	0.33 (0.31)	211 (199)	5.86 (6.22)	0.0003 (0.0013)	
S_5	($(n_O-n_N)\pi_2^*$) $(n_O+n_N)\pi_2^*$ ($(n_O+n_N)\pi_2^*$) $(n_O-n_N)\pi_2^*$ (--)	(0.18) 0.16 (0.12) 0.09 (--) 0.08 (--)	202 (194)	6.14 (6.39)	0.0000 (0.0002)	

	$(n_O+n_N)\pi_3^*$ (--)					
S_6	$(n_{N1}+n_{N2})\pi_1^*$ ($\pi_1\pi_2^*$)	0.26 (0.32)	197 (192)	6.29 (6.47)	0.0047 (0.8635)	
S_7	$\pi_1 Ryd_1$ ($(n_{N1}+n_{N2})\pi_1^*$))	0.47 (0.24)	190 (190)	6.53 (6.53)	0.0000 (0.0045)	
S_8	$\pi_1\pi_2^*$ ($\pi_1\pi_3^*$) $\pi_2\pi_1^*$	0.29 (0.45) 0.18	190 (175)	6.54 (7.10)	0.6012 (0.0160)	
S_9	$\pi_1 Ryd_2$ ($\pi_1 Ryd_1$)	0.46 (0.44)	178 (173)	6.95 (7.16)	0.0000 (0.0002)	
S_{10}	$\pi_1\pi_3^*$ ($(n_O+n_N)\pi_2^*$) ($(n_O-n_N)\pi_2^*$)	0.43 (0.19) (0.11)	177 (172)	7.02 (7.23)	0.0575 (0.0020)	

Table S2. Relative energies (in nm and eV) for the lowest lying triplet excited states of 2-oxopurine evaluated at the ground state equilibrium geometry according to the MS-CASPT2, ADC(2), CC2 and M062X methods.

	Main Configurations	Energies (nm)	Energies (eV)
	MS-CASPT2 IPEA=0.00 (0.25)		
T_1	$\pi_1\pi_2^*$ ($\pi_1\pi_2^*$)	466 (426)	2.66 (2.91)
T_2	$\pi_1\pi_1^*$ ($\pi_1\pi_1^*$)	263 (243)	4.71 (5.11)
T_3	$\pi_2\pi_2^*$ ($n_O\pi_2^*$)	259 (238)	4.79 (5.22)
	ADC(2)		
T_1	$\pi_1\pi_1^*$	425	2.92
T_2	$\pi_1\pi_2^*$	248	4.99
T_3	$\pi_2\pi_1^*$	242	5.12
	CC2		
T_1	$\pi_1\pi_1^*$	410	3.02
T_2	$\pi_1\pi_2^*$	243	5.10
T_3	$\pi_2\pi_1^*$	238	5.21
	TD-M062X (PCM)		
T_1	$\pi_1\pi_1^*$ ($\pi_1\pi_1^*$)	450 (423)	2.75(2.93)
T_2	$(n_O+n_N)\pi_1^*$ ($\pi_1\pi_2^*$)	278 (262)	4.46 (4.73)
T_3	$\pi_1\pi_2^*$ $(n_O+n_N)\pi_1^*$)	264 (262)	4.70 (4.74)

Table S3. X Y and X cartesian coordinates (in Å) for the CASSCF optimized geometries along the Potential Energy Surface of 2-oxopurine.

FC

N	2.412337	4.755862	0.423560
C	1.146177	4.522421	−0.084672
H	0.313519	4.352133	0.566818
N	1.078107	4.531399	−1.370358
C	2.384292	4.788336	−1.779115
C	2.966276	4.920714	−2.995033
N	4.304856	5.176798	−2.999668
H	4.788407	5.284113	−3.862423
C	5.120781	5.313356	−1.865556
N	4.512543	5.175739	−0.626223
C	3.246842	4.933718	−0.638531
H	2.677634	4.790189	1.379161
O	6.289575	5.539646	−2.010374
H	2.463019	4.840716	−3.937841

S_{1min}

N	2.392411	4.752057	0.436222
C	1.139973	4.520986	−0.048142
H	0.303159	4.350952	0.595981
N	1.094482	4.532297	−1.353871
C	2.383711	4.784619	−1.744819
C	2.964433	4.913925	−3.049975
N	4.326434	5.180189	−3.001330
H	4.849495	5.297433	−3.838662
C	5.030751	5.295453	−1.835354
N	4.559125	5.183377	−0.640658
C	3.199499	4.923655	−0.649798
H	2.672417	4.792246	1.387700
O	6.311714	5.546463	−2.061564
H	2.476758	4.851488	−3.995985

T_{1min}

N	2.400120	4.753248	0.441178
C	1.146550	4.521603	−0.032691
H	0.303861	4.349565	0.599429
N	1.116925	4.538990	−1.370971
C	2.366324	4.784464	−1.750119
C	2.958945	4.920563	−3.069188
N	4.323450	5.180789	−3.022540
H	4.832913	5.292835	−3.868326
C	5.098013	5.309274	−1.880584
N	4.514719	5.175936	−0.614724
C	3.221147	4.928743	−0.632887
H	2.682463	4.790905	1.393105
O	6.277932	5.536842	−1.983987
H	2.461003	4.841383	−4.007950

($S_1/T_2/T_1$)

N	2.396182	4.755560	0.438446
C	1.146305	4.514385	−0.058141
H	0.305407	4.355684	0.584977
N	1.097945	4.499390	−1.351207
C	2.401810	4.745524	−1.756070
C	2.966322	4.810891	−3.056509
N	4.336224	5.197306	−3.020127
H	4.874088	5.113985	−3.849009
C	5.007424	5.316304	−1.838759
N	4.558177	5.205557	−0.662766
C	3.206667	4.904323	−0.659924
H	2.668303	4.811645	1.387754
O	6.318729	5.626528	−2.017195
H	2.420773	5.068048	−3.941723

(S_1/S_0)

N	2.40051	4.73055	0.43927
C	1.11509	4.57436	−0.01742
H	0.25922	4.40445	0.64582
N	1.05673	4.62068	−1.34231
C	2.35060	4.81636	−1.75318
C	2.94312	5.06050	−3.10464
N	4.33820	5.29606	−2.97272
H	4.85412	5.60289	−3.78084
C	4.95625	5.25782	−1.80681
N	4.56050	5.08410	−0.63492
C	3.13503	4.84224	−0.65169
H	2.70420	4.75581	1.40535
O	6.34998	5.39764	−2.22907
H	2.68079	4.48170	−3.99705