

Supplementary Information

Photodynamical simulations of cytosine: characterization of the ultra fast bi-exponential UV deactivation

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Table S1: Time constants for deactivation of UV-excited cytosine and cytosine derivatives.

Molecule	Medium	pH	Tech	pump (nm)	probe (nm)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	Ref.
dC	W	7	F	260	330		0.76±0.12		1
dCMP	W	7	F	260	330		0.95±0.12		
C	V		A	267	800		3.2		2
C	W	7	A	267	320		1.1±0.2		3
C	W	7	F	267	330	0.20±0.02	1.30±0.07		
dC	W	7	F	267	330	0.18±0.02	0.92±0.06		
dCMP	W	7	F	267	330	0.27±0.02	1.4±0.2		
C	W	6.8	A	265	570		1.0±0.2		4
C-	W	13	A	265	570			13.3±0.4	
dC+	W	0.08	A	265	570		0.63±0.06		
dC	W	6.8	A	265	570		1.0±0.1		
5FC	W	6.8	A	265	570			88±5	
5mC+	W	1.5	A	265	570			2.57±0.22	
5mC	W	6.8	A	265	570			7.2±0.4	
5mC-	W	13	A	265	570			250±30	
5mdC	W	6.8	A	265	570			7.2±0.2	
4acC	W	6.8	A	265	570			280±30	
C	V		A	250	200	<0.05	0.82	3.2	5
C	V		A	267	2×400	0.16±0.02	1.86±0.19		6
C	V		A	260	800	0.12	3.8		7
C	V		A	267	800	0.21	2.2	long	
C	V		A	270	800	0.22	2.3	19	
C	V		A	280	800	<0.1	1.2	55	
C	V		A	290	800	<0.1	1.1	≥150	
C	W	6.8	A	263	570		0.72		8
5FC	W	6.8	A	263	570,600,630			73±4	
5FC	Ethanol		A	263	570			73±4	
5FC	DMSO		A	263	570			73±4	

C – cytosine; dC – cytidine; dCMP – cytidine monophosphate; 5FC – 5-Fluorocytosine; 5mC – 5-methylcytosine; 5mdC – 5-methylcytidine; 4acC – N4-acetylcytosine; W – water; V – vapor; DMSO – dimethylsulfoxide; A – absorption; F – Fluorescence

Table S2 – Correspondence between the several notations for the conical intersections in cytosine.

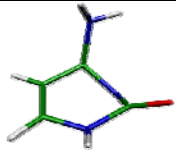
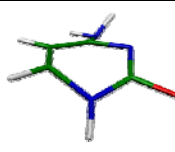
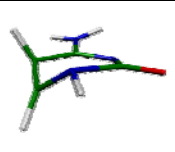
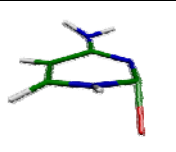
Ref.				
Present work	<i>oop</i> -NH ₂	<i>semi-planar</i>	<i>C6-puckered</i>	<i>oop</i> -O
8, 9	(GS/n _N ,π*) _{CI}	(GS/n _O ,π*) _{CI}		
10	(OP) _X		(Eth) _X	
11	(n _N ,π*) _X	(n _O ,π*) _X	(Eth) _X	
12	n _N /S ₀	n _O /S ₀	ππ/S ₀	
13	(gs/n _N π*) _{CI}	(gs/n _O π*) _{CI}	(gs/ππ*) _{CI}	
14			¹ ππ*/S ₀	
15			ETH	
16			(π-π*) _{CI}	
17, 18	R _x (<i>ci01</i>) _{sofa}	R _x (<i>ci01</i>) [?]	R _x (<i>ci01</i>) _{twist}	
19	CI _{c01β}		CI _{c01α}	

Fig. S1 – Molecular orbitals at the SA-4-CASSCF(14,10)/6-31G* level of calculation for the ground state minimum and the S_1 ($n\pi^*$) minimum geometries.

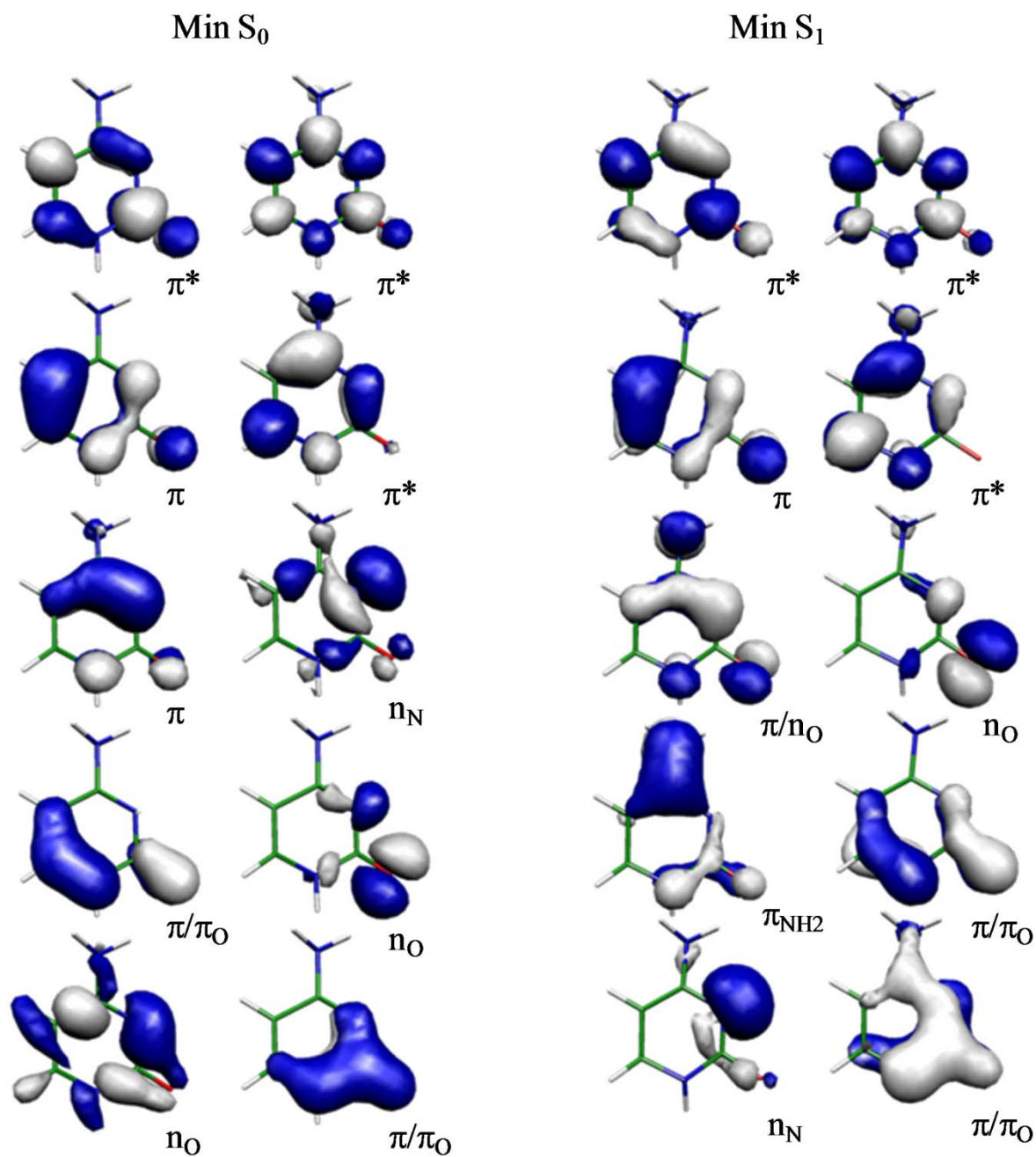
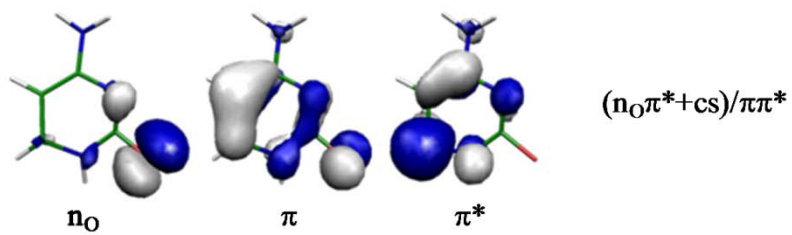
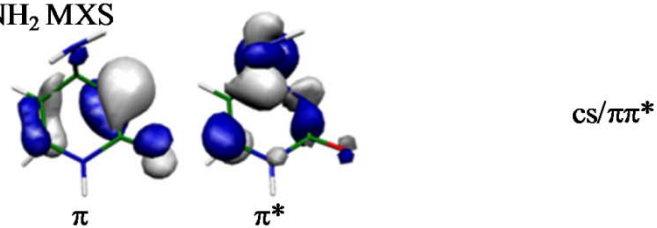


Fig. S2 – Molecular orbitals and main electronic configurations of the MXSs.

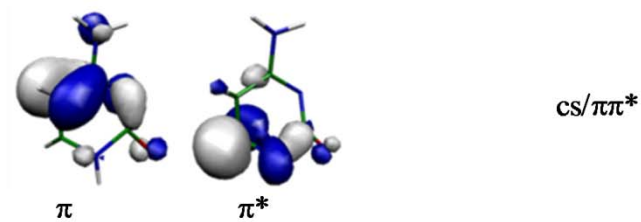
semi-planar MXS



oop-NH₂ MXS



C6-puckered MXS



oop-O MXS

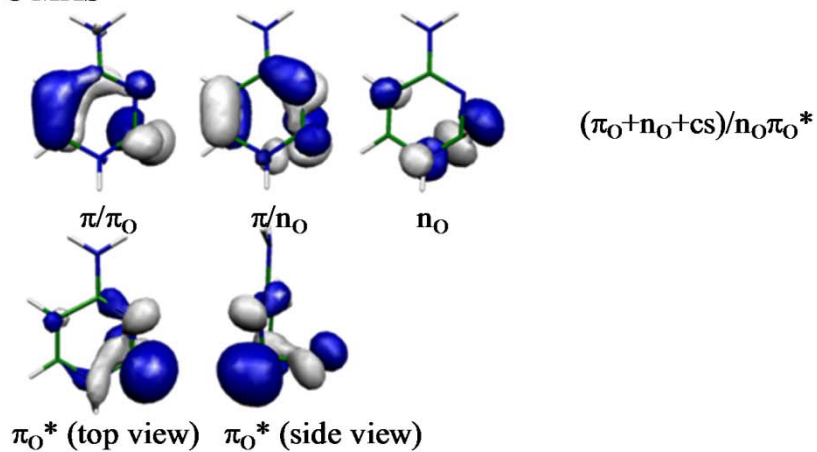


Fig. S3 – Geometry of four minima on the S_1/S_0 crossing seam of cytosine optimized at SA-4-CASSCF(14,10)/6-31G* level.

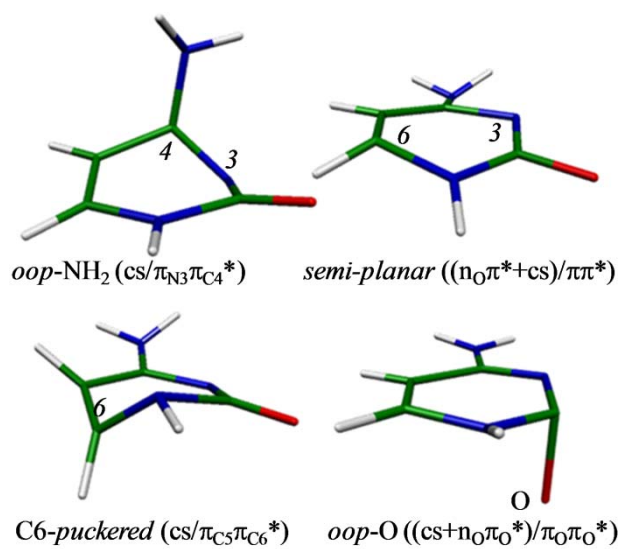
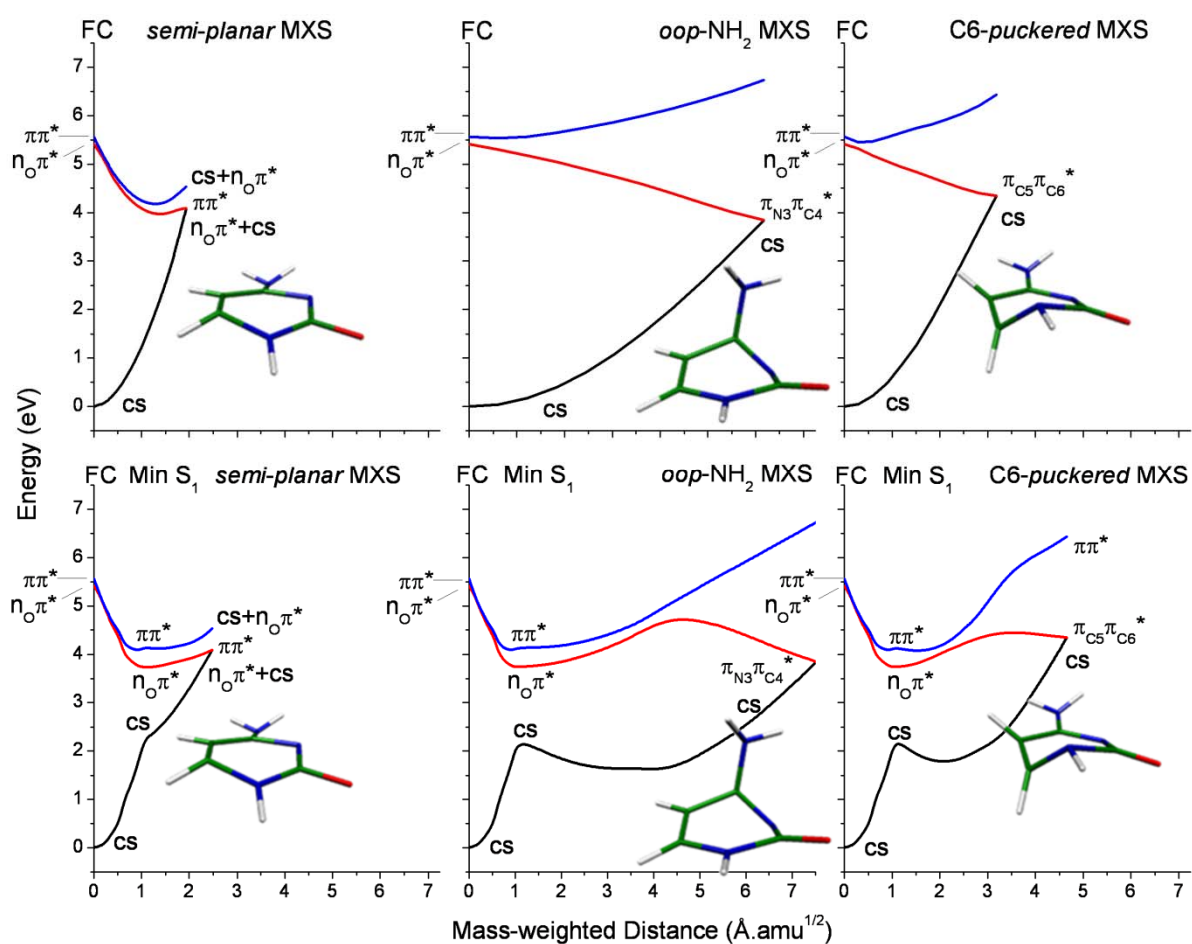


Fig. S4 – Linearly interpolated pathways between the Franck-Condon (FC) region and the three lowest-energy MXSs (Top) and between the FC region, the S_1 minimum and the three MXSs (bottom). Computed at SA-4-CASSCF(14,10)/6-31G* level. Only three states are shown for clarity.



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Cartesian coordinates (Å) of the ground state minimum, of the first excited state minimum and of the minima on the crossing seam for cytosine optimized at CASSCF and MR-CISD levels.

SA-4-CASSCF(14,10)/6-31G*

Min S₀

N	-0.010527	0.022158	0.069853
N	2.359536	-0.001439	0.055202
N	-1.163924	-0.027506	2.054645
C	1.169017	-0.002461	-0.669276
C	2.405775	-0.006236	1.417830
C	1.261710	-0.000267	2.125954
C	0.023067	0.014593	1.350128
O	1.188206	-0.014775	-1.868864
H	3.196209	-0.011244	-0.483239
H	3.380643	-0.021353	1.864034
H	1.249297	-0.026789	3.196863
H	-1.172926	0.460374	2.923688
H	-1.964927	0.162723	1.490985

Min S₁

N	1.222272	-0.667907	-0.031318
N	2.119341	0.962047	1.421828
N	-1.087576	-0.938657	-0.323974
C	2.176923	-0.098443	0.565626
C	0.851353	1.529059	1.685734
C	-0.246162	0.937857	1.030539
C	-0.063368	-0.174315	0.239500
O	3.446488	-0.489729	0.343746
H	2.835242	1.033217	2.109625
H	0.844718	2.527453	2.073303
H	-1.226332	1.353073	1.175540
H	-1.930530	-0.427972	-0.483543
H	-0.789413	-1.398582	-1.159052

MXS *semi-planar*

N	1.247339	-0.592949	-0.133646
N	2.066006	0.862938	1.506969
N	-1.059559	-0.998518	-0.246775
C	2.132067	-0.105604	0.584894
C	0.914214	1.663111	1.550634
C	-0.261791	0.954998	0.994133
C	-0.082442	-0.132029	0.234524
O	3.498054	-0.380462	0.460620
H	2.808370	0.960221	2.162539
H	0.823206	2.248635	2.444624
H	-1.245911	1.304670	1.245930
H	-1.976884	-0.605441	-0.263555
H	-0.813423	-1.377275	-1.137704

MXS *oop*-NH₂

N	0.051029	-0.342346	0.278564
N	2.275978	0.151918	0.109732
N	-0.540695	1.515912	1.716264
C	1.070180	0.186462	-0.553925
C	2.367623	-0.121132	1.487814
C	1.257521	-0.082631	2.273556
C	0.013329	0.242471	1.561057
O	0.910395	0.539787	-1.678633
H	3.087916	0.373819	-0.419085
H	3.354987	-0.318641	1.854164
H	1.298798	-0.217438	3.336037
H	0.112224	2.267271	1.817670
H	-1.265038	1.737951	1.066338

MXS C6-*puckered*

N	-0.109425	0.241573	0.163502
N	2.296317	0.662399	0.546984
N	-1.237947	-0.843015	1.860263
C	0.956766	0.878816	-0.280732
C	2.316857	-0.638741	0.846211
C	1.189721	-0.996596	1.720301
C	-0.034812	-0.573210	1.243741
O	1.145993	1.579309	-1.232401
H	3.032152	0.980016	-0.056162
H	2.829375	-1.351072	0.215962
H	1.343230	-1.079500	2.781005
H	-1.181639	-1.274039	2.756465
H	-1.909001	-0.107473	1.807021

MXS *oop*-O

N	-0.058584	0.077461	0.066490
N	2.359818	0.051992	0.051917
N	-1.172304	-0.058811	2.054599
C	1.152103	-0.018492	-0.565087
C	2.389688	0.042736	1.459609
C	1.234800	-0.033180	2.128728
C	-0.024634	-0.020881	1.342000
O	1.197972	-1.649653	-0.575425
H	3.121291	0.453040	-0.450232
H	3.355171	0.010127	1.923275
H	1.204078	-0.111436	3.197888
H	-1.174139	0.074029	3.037704
H	-2.035077	0.037488	1.568978

MR-CISD(6,5)/SA-4-CASSCF(14,10)/6-31G*

Min S₀

N	-0.018758	0.015852	0.068684
N	2.349142	-0.005499	0.066805
N	-1.166998	-0.030522	2.053566
C	1.163668	0.004501	-0.673191
C	2.401890	-0.008329	1.406587
C	1.261977	0.002463	2.130907
C	0.033803	0.016547	1.376105
O	1.195069	0.015252	-1.861245
H	3.173164	-0.009309	-0.479576
H	3.361328	-0.024384	1.857765
H	1.280338	-0.020665	3.195543
H	-1.190530	0.427902	2.943044
H	-1.953096	0.181670	1.468460

Min S₁

N	1.224434	-0.617009	-0.070442
N	2.112710	0.923626	1.465957
N	-1.088683	-0.960521	-0.296361
C	2.184587	-0.085400	0.563373
C	0.850465	1.531303	1.658849
C	-0.244335	0.954491	1.011358
C	-0.071179	-0.184740	0.260135
O	3.406914	-0.541636	0.297950
H	2.880652	1.081195	2.066285
H	0.830838	2.467893	2.154604
H	-1.202587	1.406496	1.132825
H	-1.933049	-0.450540	-0.467871
H	-0.779023	-1.419105	-1.133052

MXS *semi-planar*

N	1.275659	-0.410674	-0.229806
N	2.074143	0.783937	1.619872
N	-0.991280	-1.108125	-0.145433
C	2.158023	-0.061633	0.573369
C	0.938866	1.668600	1.447971
C	-0.275099	0.996453	0.976497
C	-0.072854	-0.097353	0.216732
O	3.461898	-0.478820	0.408595
H	2.388628	0.479540	2.505875
H	0.909269	2.491529	2.116006
H	-1.239025	1.356276	1.235665
H	-1.925648	-0.870010	0.133747
H	-0.979457	-1.265454	-1.138534

MXS *oop-NH₂*

N	0.073557	-0.348034	0.256670
N	2.301586	0.066198	0.082115
N	-0.588471	1.493534	1.728981
C	1.085129	0.267145	-0.530916
C	2.373330	-0.137255	1.477434
C	1.272294	-0.028664	2.265259
C	0.023714	0.244325	1.567371
O	0.922357	0.806921	-1.585633
H	3.090102	0.449274	-0.380366
H	3.351217	-0.348516	1.853680
H	1.345677	-0.089469	3.323134
H	0.037754	2.282533	1.742639
H	-1.360197	1.648126	1.112760

MXS C6-*puckered*

N	-0.132435	0.293465	0.211341
N	2.318361	0.580827	0.455612
N	-1.215007	-0.864954	1.846582
C	0.965019	0.938352	-0.236597
C	2.301941	-0.714459	0.861656
C	1.215035	-0.974561	1.788166
C	-0.052962	-0.535594	1.249995
O	1.074767	1.735787	-1.107639
H	3.040240	0.835796	-0.195901
H	2.858794	-1.465983	0.352577
H	1.370120	-0.643248	2.800770
H	-1.191621	-1.512923	2.573506
H	-1.997109	-0.320603	1.610768

MXS *oop-O*

N	-0.089779	-0.086244	0.077185
N	2.335327	0.166375	0.102879
N	-1.166465	0.024387	2.083651
C	1.089145	-0.069206	-0.608373
C	2.411919	-0.021738	1.443920
C	1.230460	-0.071848	2.113141
C	-0.023383	0.021562	1.361609
O	1.767737	-1.188123	-1.063036
H	3.093685	0.538578	-0.411741
H	3.355623	-0.203483	1.901222
H	1.204465	-0.214366	3.172212
H	-1.175202	0.388651	3.007165
H	-2.006983	0.145047	1.553556