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SUPPORTING INFORMATION

On the Propensity of Formation of Cyclobutane Dimers in Face-to-Face and Face-to-Back Uracil Stacks in Solution

Branislav Milovanović[#,†] Jurica Novak[#,‡,¶] Mihajlo Etinski,[†] Wolfgang Domcke,[§] and Nađa Došlić[*,‖]

†*Faculty of Physical Chemistry, University of Belgrade, 10000 Belgrade, Serbia*

‡*Department of Biotechnology, University of Rijeka, HR-51000 Rijeka, Croatia*

¶*Scientific and Educational Center "Biomedical Technologies" School of Medical Biology, South Ural State University, RU-454080, Chelyabinsk, Russia*

§*Department of Chemistry, Technical University of Munich, Garching, Germany*

‖*Department of Physical Chemistry, Ruđer Bošković Institute, HR-10000 Zagreb, Croatia*

E-mail: nadja.doslic@irb.hr

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Table S1 Relevant structural parameters of the minimum energy structures of F2F stacked uracil dimers obtained with MP2/cc-pVDZ and MP2/aug-cc-pVDZ in vacuum and with the COSMO solvation model. The slide, rise, separation and twist coordinates are defined in Figure S1, while d_1 and d_2 are respectively the $C5' \cdots C6''$ and $C6' \cdots C5''$ distances and α is the angle between the C5′=C6′ and C5″=C6″ bonds. Cartesian coordinates of F2F stacked uracil dimers obtained with MP2/cc-pVDZ and MP2/aug-cc-pVDZ in vacuum and with the COSMO solvation model are given in Tables S5-S8.

		slide	rise	separation	twist	d_1	d_2	α
MP2/cc-pVDZ	vacuum	0.52	3.23	3.28	71	3.67	3.65	19
	COSMO	0.62	3.23	3.29	72	3.63	3.64	19
MP2/aug-cc-pVDZ	vacuum	0.41	3.13	3.15	73	3.49	3.49	20
	COSMO	0.74	3.08	3.17	97	3.59	3.59	45

Table S2 Relevant structural parameters of the minimum energy structures of F2B stacked uracil dimers obtained with MP2/cc-pVDZ and MP2/aug-cc-pVDZ in vacuum and with the COSMO solvation model. The slide, rise, separation and twist coordinates are defined in Figure S1. In F2B d_1 and d_2 are the $C5' \cdots C5''$ and $C6' \cdots C6''$ distances, respectively and α is the angle between the two bonds. Cartesian coordinates of F2F stacked uracil dimers obtained with MP2/cc-pVDZ and MP2/aug-cc-pVDZ in vacuum and with the COSMO solvation model are given in Tables S9-S12.

		slide	rise	separation	twist	d_1	d_2	α
MP2/cc-pVDZ	vacuum	0.07	3.15	3.15	66	3.89	4.11	65
	COSMO	0.75	3.06	3.15	69	3.65	3.70	68
MP2/aug-cc-pVDZ	vacuum	0.34	3.01	3.03	67	3.57	3.88	66
	COSMO	0.95	2.98	3.13	64	3.38	3.77	62

Table S3 Vertical excitation energies and oscillator strengths (in parentheses) of the six lowest singlet states of F2F an F2B stacked uracil dimers computed with ADC(2)/aug-cc-pVDZ. The excitation energies were computed at the MP2/aug-cc-pVDZ minimum of F2F and F2B optimized in the gas phase (E^{gas}) and in water solution (E^{cosmo}). The spectral assignment is given in Table 1.

	F2F		F2B	
S_n	E^{gas}	E^{cosmo}	E^{gas}	E^{cosmo}
S_1	4.47 (0.000)	4.83 (0.022)	4.38 (0.000)	4.77 (0.000)
S_2	4.48 (0.000)	4.83 (0.003)	4.41 (0.000)	4.78 (0.000)
S_3	4.74 (0.022)	4.89 (0.055)	4.99 (0.088)	4.87 (0.104)
S_4	5.06 (0.254)	4.90 (0.252)	5.13 (0.192)	4.99 (0.260)
S_5	5.61 (0.000)	5.93 (0.064)	5.57 (0.000)	5.81 (0.046)
S_6	5.65 (0.000)	5.99 (0.000)	5.70 (0.001)	5.84 (0.016)

Table S4 Vertical excitation energies and oscillator strengths (in parentheses) of the six lowest singlet states of F2F an F2B stacked uracil dimers computed with ADC(2)/aug-cc-pVDZ//MP2/cc-pVDZ. The excitation energies were computed at the MP2/cc-pVDZ minimum of F2F and F2B optimized in the gas phase (E^{gas}) and in water solution (E^{cosmo}). The spectral assignment is given in Table 1.

	F2F		F2B	
S_n	E^{gas}	E^{cosmo}	E^{gas}	E^{cosmo}
S_1	4.59 (0.000)	4.81 (0.022)	4.50 (0.000)	4.91 (0.000)
S_2	4.60 (0.000)	4.92 (0.000)	4.53 (0.000)	4.94 (0.000)
S_3	4.89 (0.023)	4.92 (0.000)	5.09 (0.092)	4.96 (0.105)
S_4	5.13 (0.260)	5.06 (0.367)	5.20 (0.198)	5.04 (0.273)
S_5	5.74 (0.001)	6.03 (0.004)	5.72 (0.000)	5.93 (0.075)
S_6	5.77 (0.000)	6.03 (0.025)	5.77 (0.000)	6.01 (0.083)

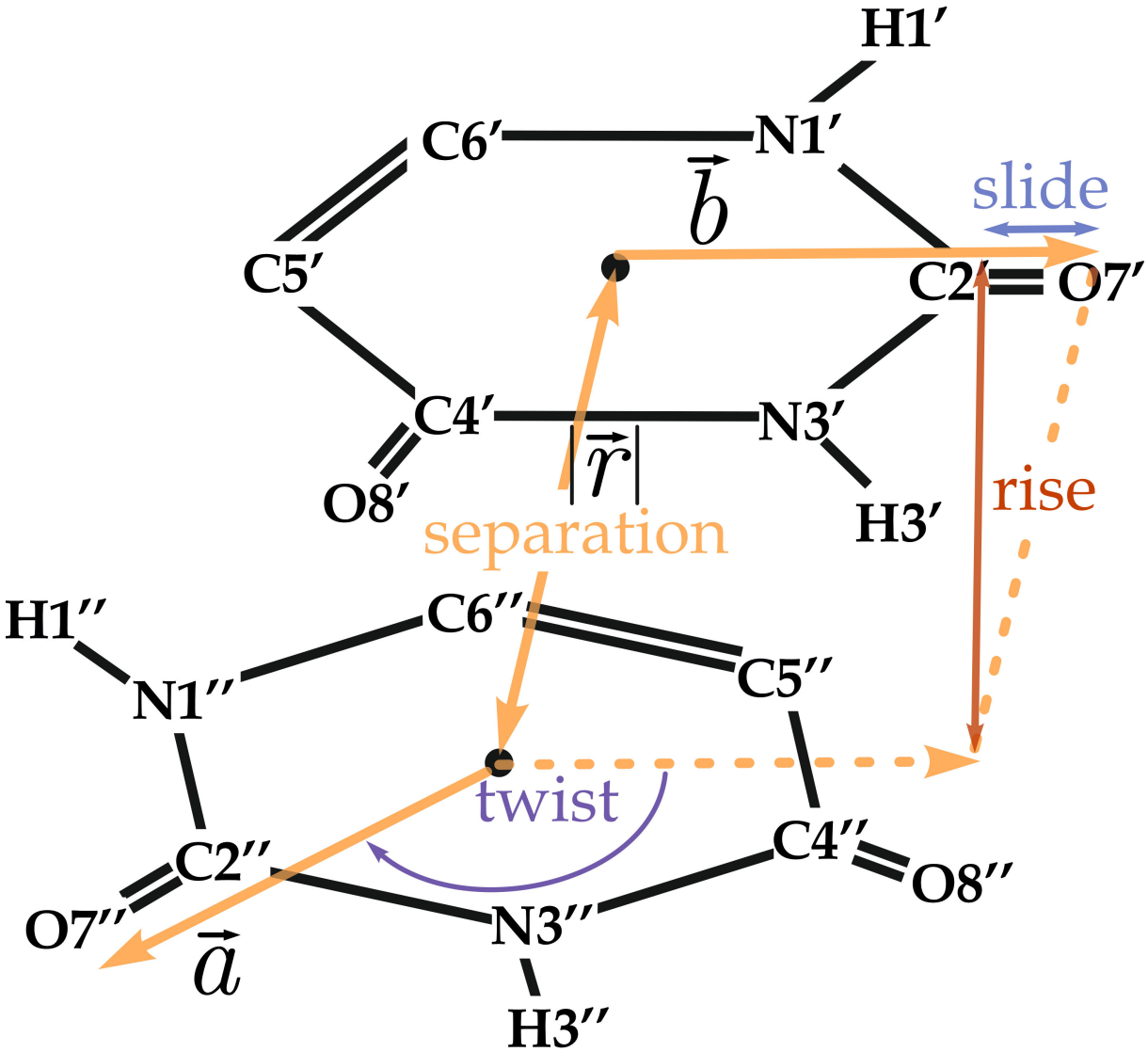

Figure S1 Definition of the slide, rise, separation and twist coordinates. Black circles indicate the midpoints of the base rings. U-U separation is defined as the length of the vector $\vec{r}$ connecting the geometrical centers of uracil rings. Rise and slide coordinates are defined as the vertical and horizontal separation between ring's midpoints, respectively. The twist angle is the angle between vector $\vec{a}$ belonging to the lower uracil and a projection of the vector $\vec{b}$ on the plane defined by the atoms of the lower uracil ring.

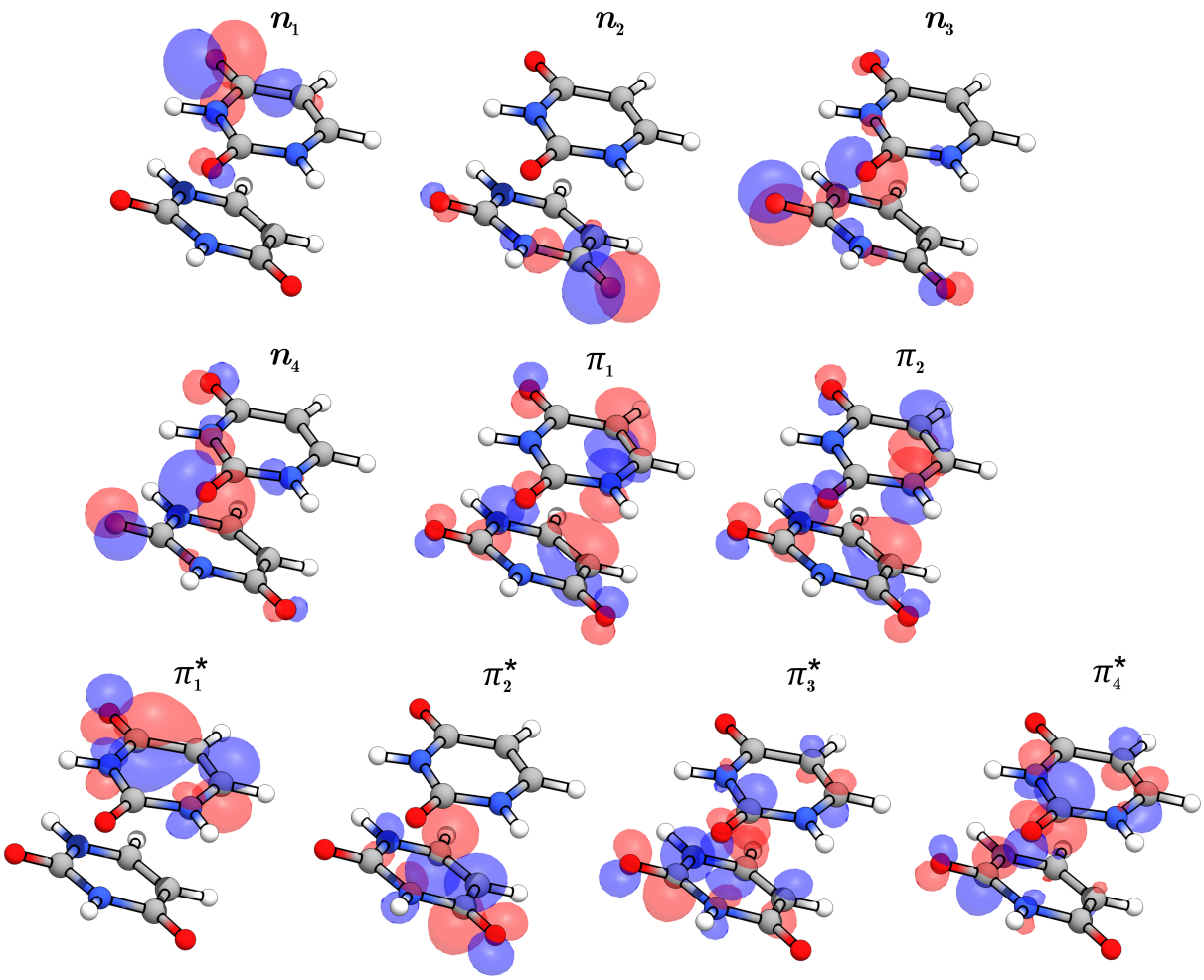

Figure S2 Dominant hole and particle NTOs contributing to the six lowest transitions of F2F. The spectral assignment is given in Table 1.

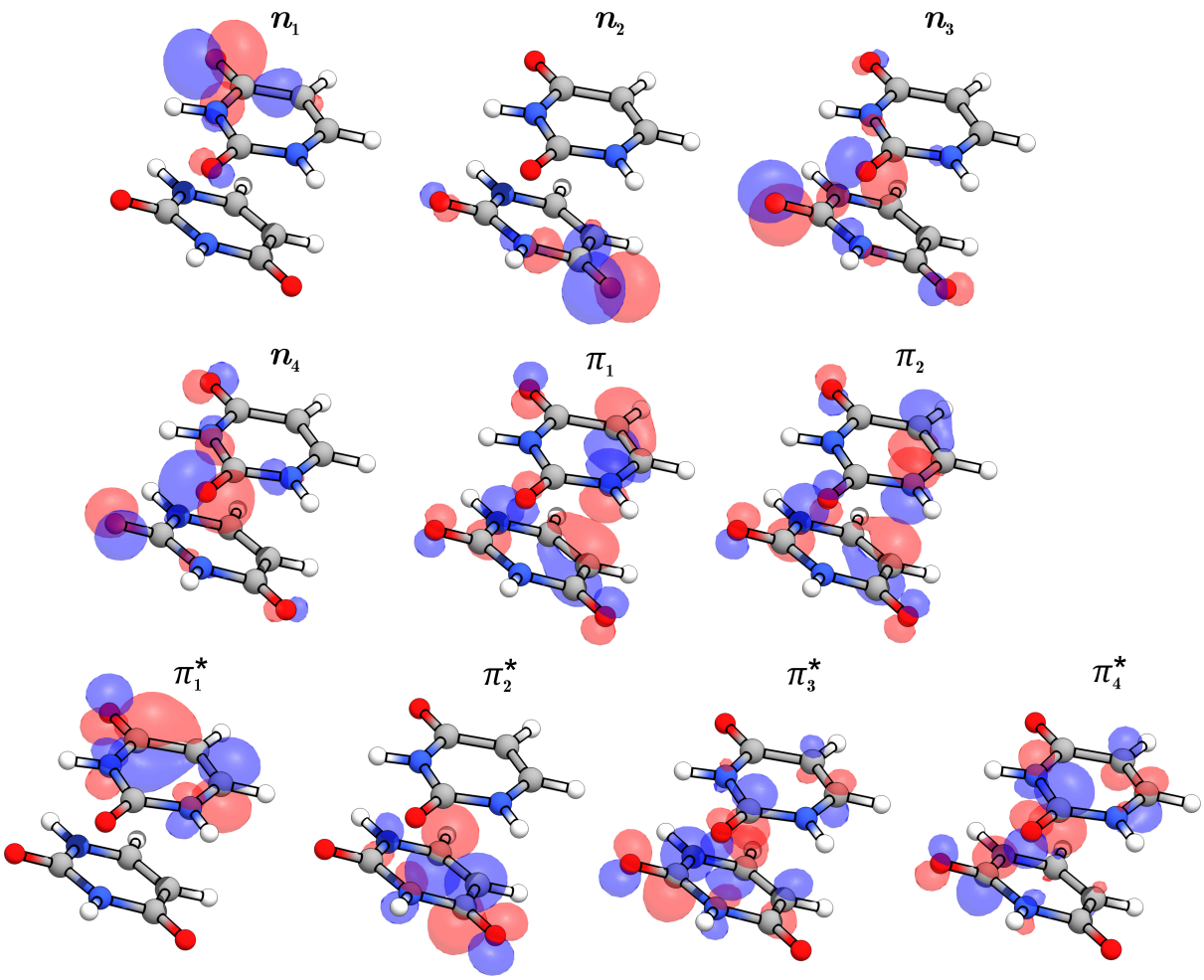

Figure S3 Dominant hole and particle NTOs contributing to the six lowest transitions of F2B. The spectral assignment is given in Table 1.

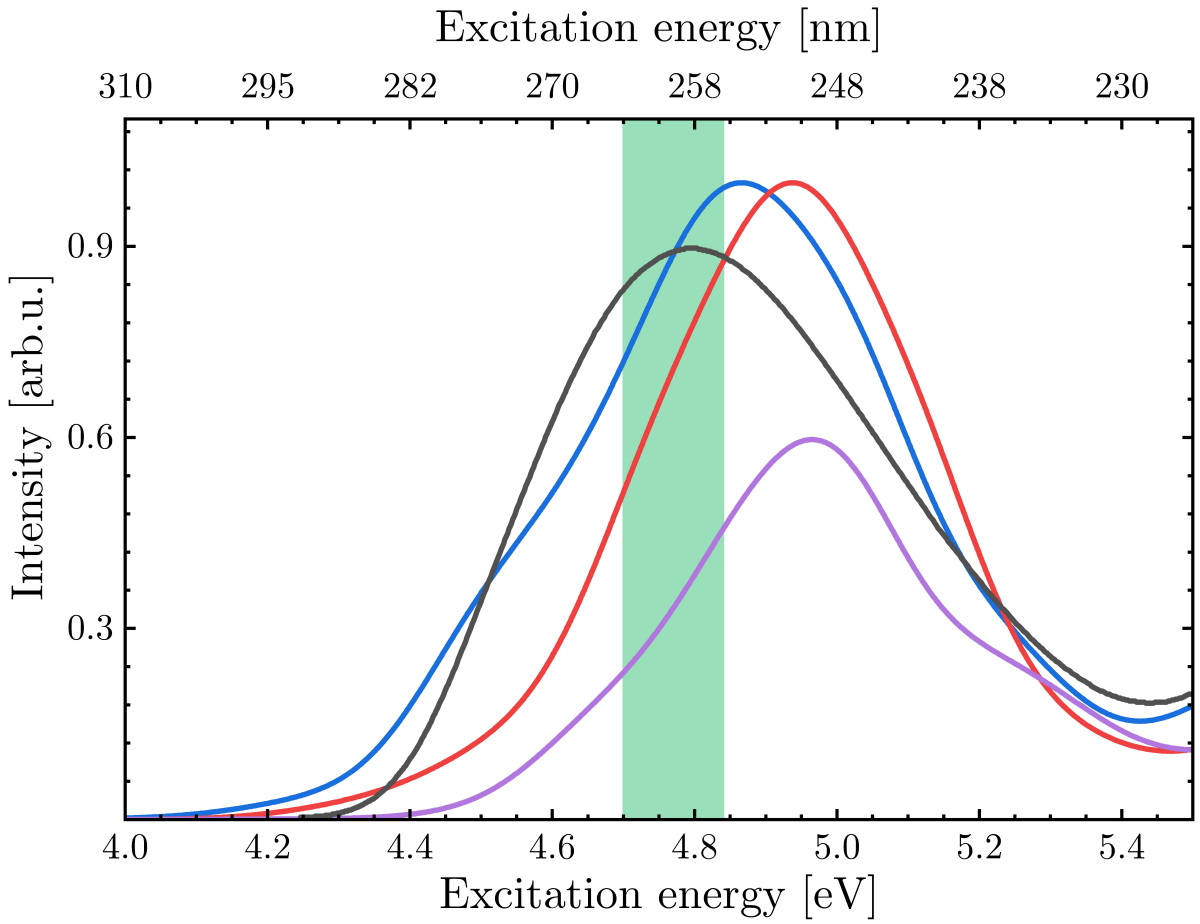

Figure S4 Comparison of the experimental absorption spectrum of uracil in water (black) of Du *et al.* with the computed spectra of F2F10W (red), F2B10W (blue) and U6W (purple). The shaded area denotes the excitation window from which the trajectories were launched. For details see Sec. 2.3.

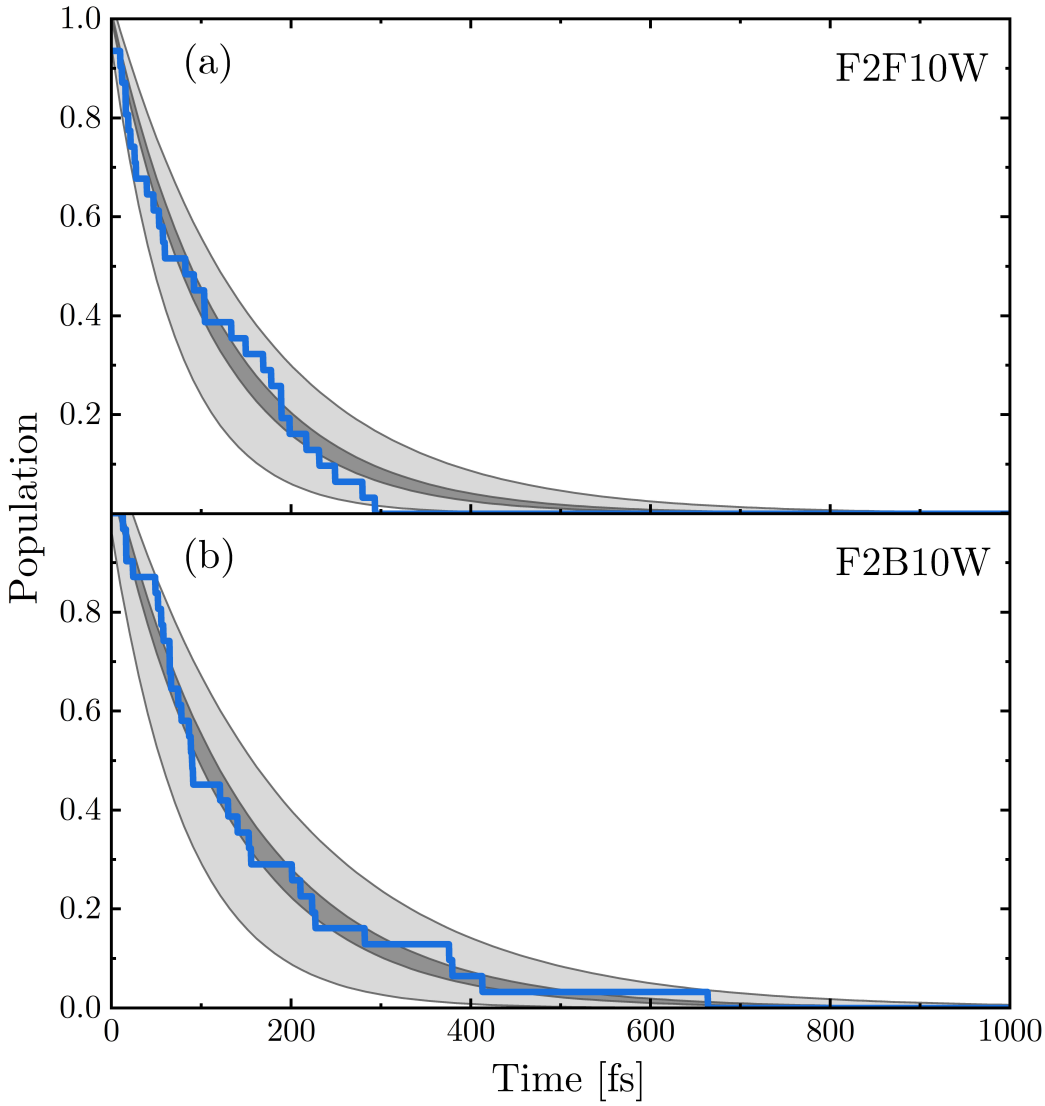

Figure S5 Average diabatic population of the bright $\pi\pi^*$ state (blue) for F2F (a) and F2B (b) dimer. Average diabatic populations are obtained using 5000 bootstrap resamples from the original set of 31 NAD trajectory for each dimer. Dark grey and gray areas represent 95 % confidence and 95 % prediction intervals, respectively. Considering the 95 % confidence interval the average decay constants of the $\pi\pi^*$ state are 118±9 fs and 150±10 fs for F2F and F2B dimer, respectively. The 95 % prediction interval yields 120±50 fs and 150±50 fs lifetimes for F2F and F2B dimer, respectively.

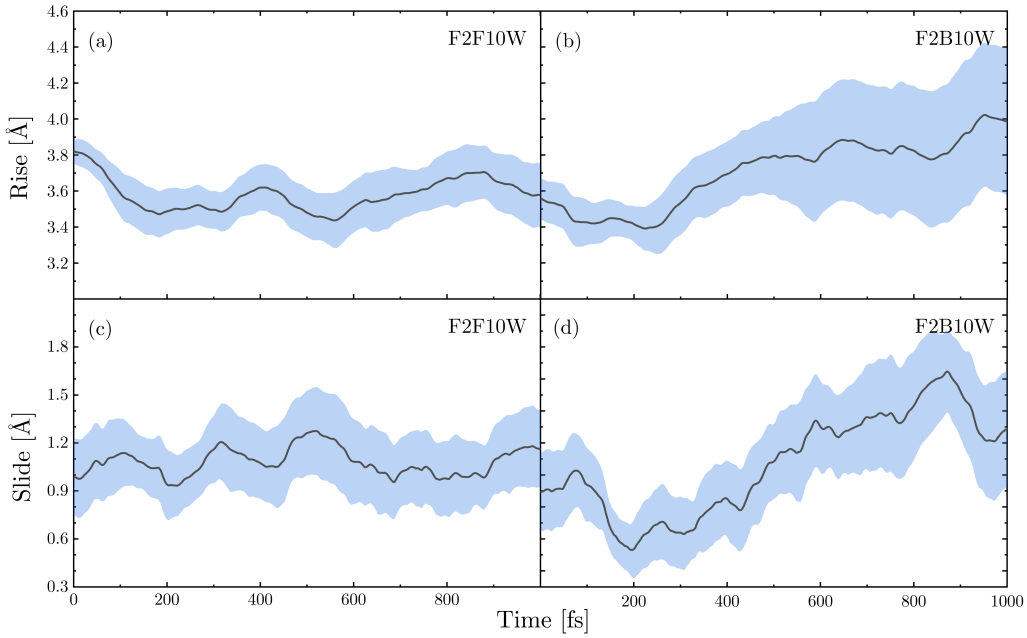

Figure S6 The evolution in time of the rise (a), (b) and slide (c), (d) coordinates in F2F10W (a and c) and F2B10W (b and d) averaged over trajectories that remained in the nπ^* state. The black lines are the mean values of the rise and slide coordinates. The blue shaded areas are the 90 % confidence interval margin of errors.

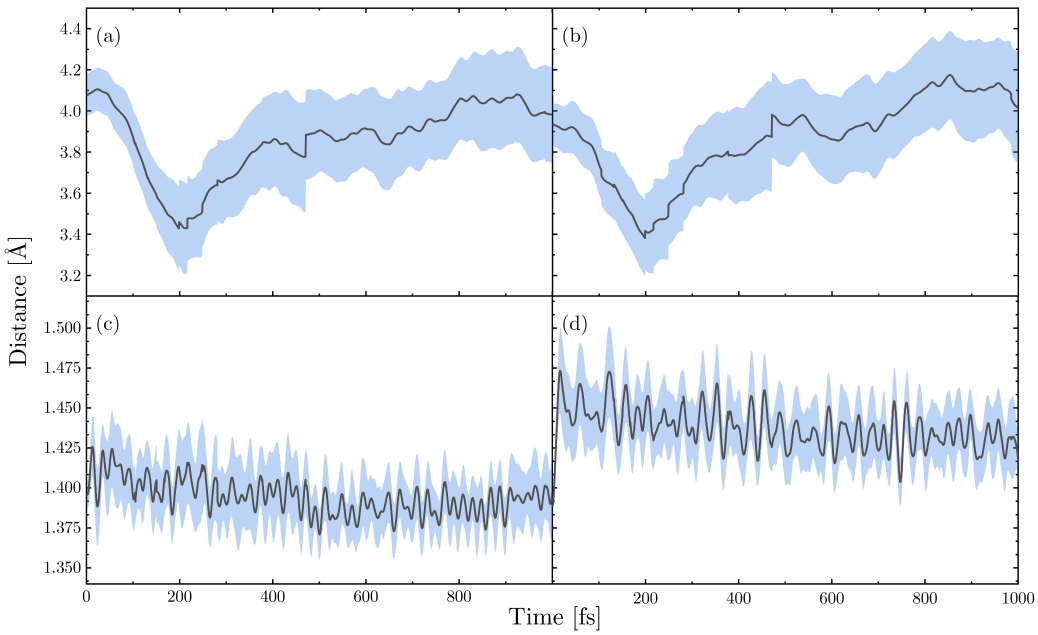

Figure S7 The evolution in time of the C6′ ··· C5″ (a) and C5′ ··· C6″ (b) distances and C5″-C6″ (c) and C5′-C6′ (d) bond lengths in F2F10W. The black lines are the mean values of the coordinates averaged over all trajectories. The blue shaded areas are the 90 % confidence interval margin of errors.

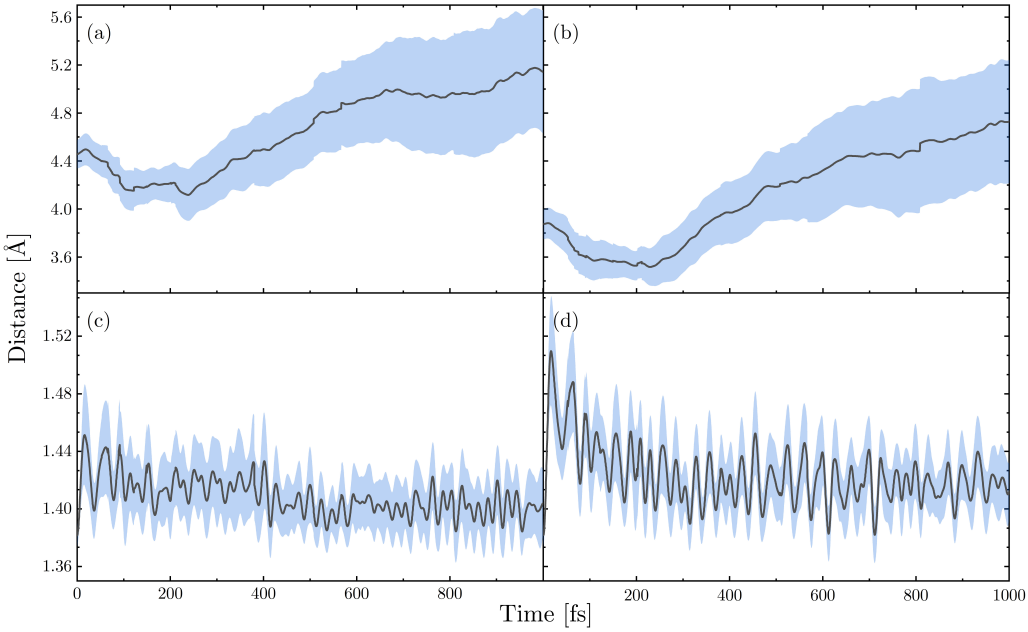

Figure S8 The evolution in time of the C6′ ··· C5″ (a) and C5′ ··· C6″ (b) distances and C5″-C6″ (c) and C5′-C6′ (d) bond lengths in F2B10W. The black lines are the mean values of the coordinates averaged over all trajectories. The blue shaded areas are the 90 % confidence interval margin of errors.

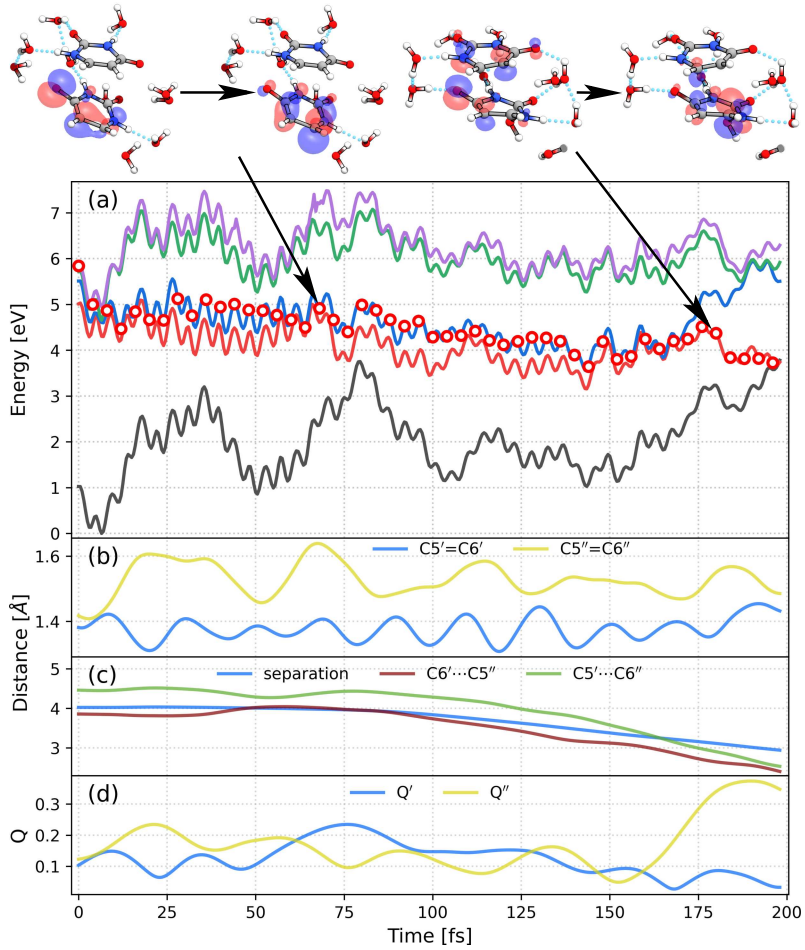

Figure S9 Time evolution of the energies of the first four excited singlet states (S_1 - red, S_2 - blue, S_3 - green and S_4 - purple lines) and the ground state (S_0 - black line) for a selected pro-reactive trajectory of F2F10W. The red dots indicate the populated state at a given time. The trajectory ends in a dimerization-like S_1/S_0 CoIn. The insets show the dominant NTO pairs at ≈70 and 175 fs (a). Time dependence of the C5′-C6′ and C6″-C5″ bond lengths (b), the separation distance between the two rings and the $C5' \cdots C6''$ and $C6' \cdots C5''$ distances (c) and the puckering parameters Q' and Q'' of the two uracil rings (d).

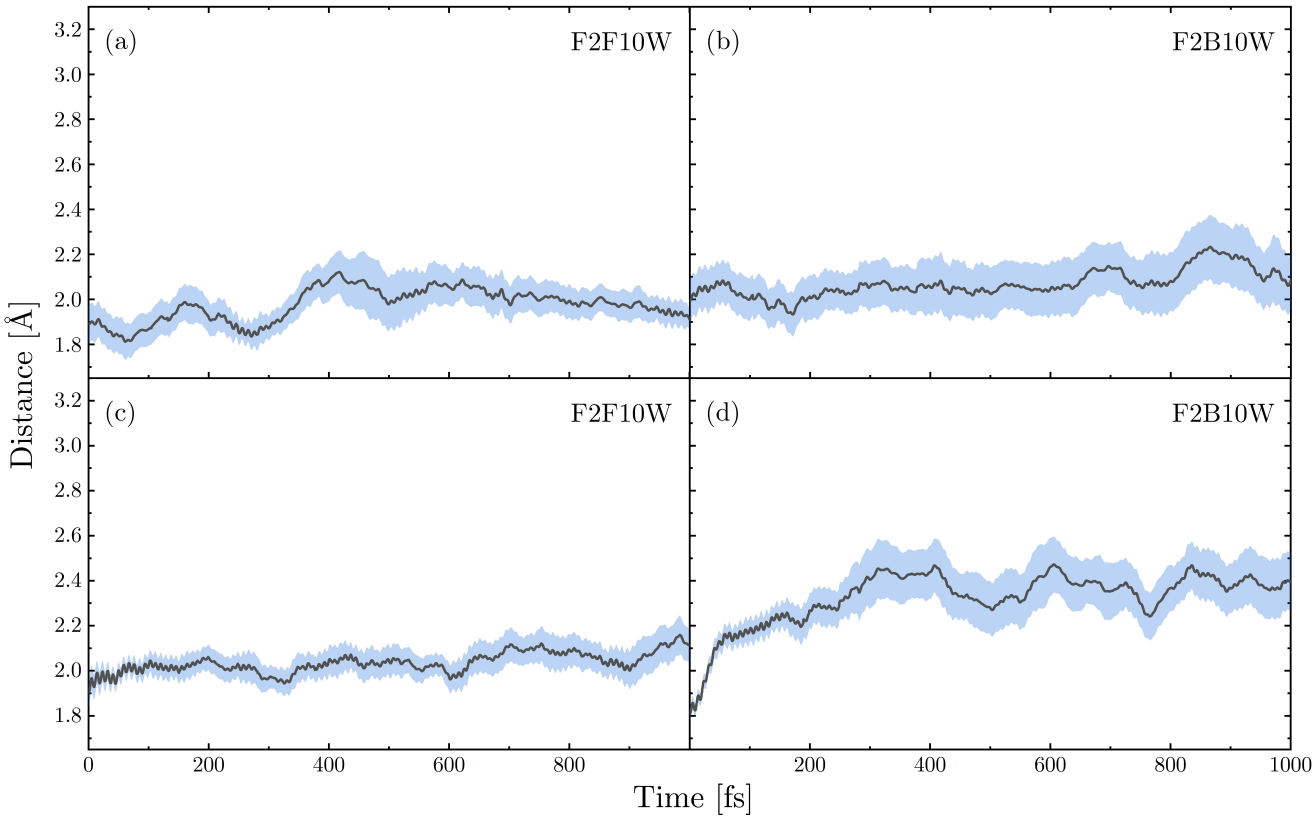

Figure S10 Time evolution of the hydrogen bond lengths for F2F dimer averaged over all trajectories. The black lines represent mean values of the (a) N1-H1$\cdots$OH$_2$, (b) N3-H3$\cdots$OH$_2$, (c) C2=O7$\cdots$HOH and (d) C4=O8$\cdots$HOH hydrogen bond lengths. The blue shaded areas are the 90 % confidence interval margin of errors.

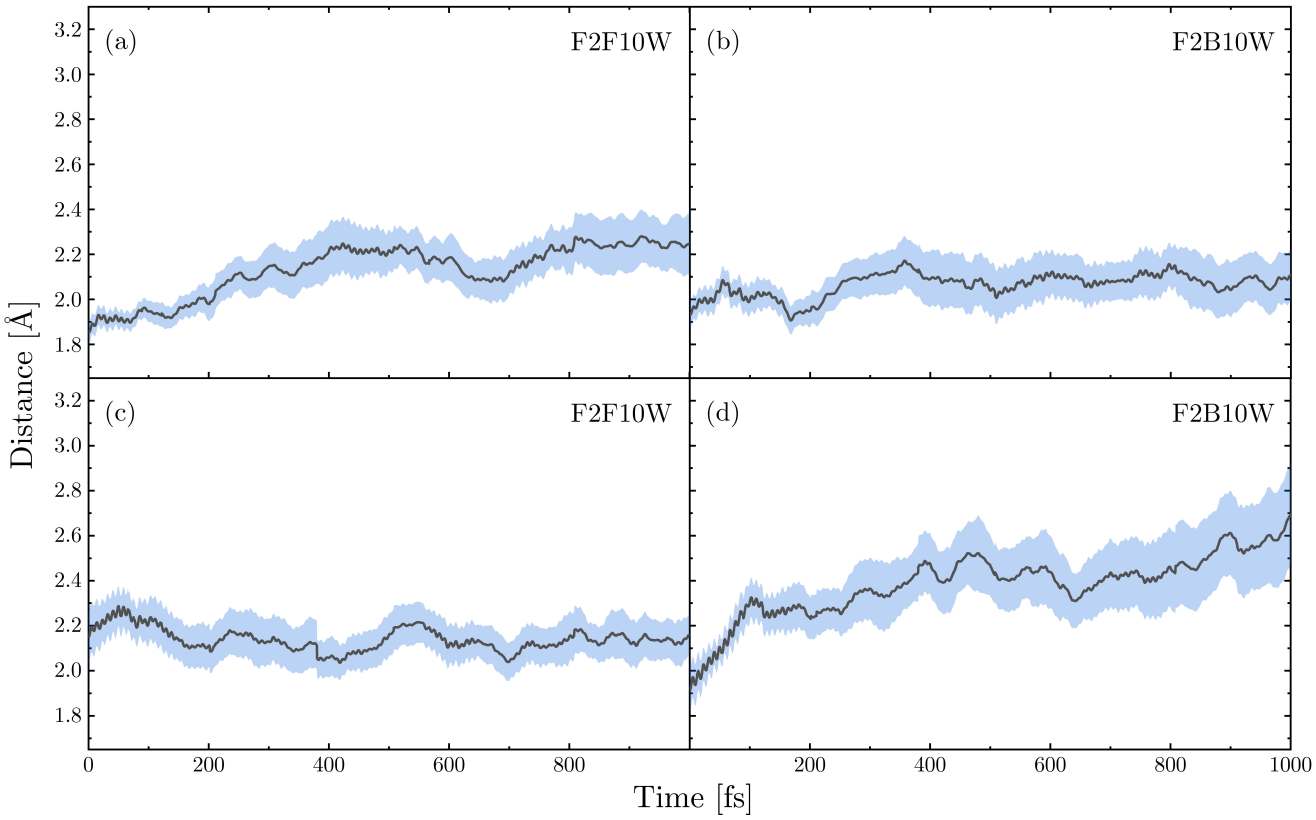

Figure S11 Time evolution of the hydrogen bond lengths for F2B dimer averaged over all trajectories. The black lines represent mean values of the (a) N1-H1$\cdots$OH$_2$, (b) N3-H3$\cdots$OH$_2$, (c) C2=O7$\cdots$HOH and (d) C4=O8$\cdots$HOH hydrogen bond lengths. The blue shaded areas are the 90 % confidence interval margin of errors.

Table S5 MP2/cc-pVDZ optimized structure of F2F stacked uracil dimer in the gas phase.

O	2.0870488	0.3564412	-1.8106673
C	1.8305884	0.1883622	-0.6289146
N	1.8963958	1.2084397	0.3141546
H	2.0532593	2.1347553	-0.0720087
N	1.4394951	-1.0284379	-0.0832324
H	1.2997457	-1.7709168	-0.7704293
C	1.4885487	1.0609241	1.6193091
H	1.5478565	1.9615705	2.2344518
C	0.9277642	-1.2794902	1.2056844
O	0.4340227	-2.3661278	1.4857163
C	1.0454088	-0.1312091	2.1028506
H	0.7243755	-0.2415822	3.1375924
O	-0.8779616	-1.5975113	-2.1185332
C	-1.2700463	-0.7859044	-1.2955546
N	-1.0073465	0.5773524	-1.3607351
H	-0.3796453	0.8473936	-2.1198084
N	-2.0289241	-1.1369081	-0.1842748
H	-2.1431753	-2.1362407	-0.0444911
C	-1.2432817	1.5578434	-0.3770791
O	-0.7779195	2.6867134	-0.4901657
C	-2.3854946	-0.2484523	0.8028347
H	-2.9485843	-0.6735147	1.6366270
C	-2.0560995	1.0700122	0.7354191
H	-2.3386551	1.7679218	1.5220986

Table S6 MP2/cc-pVDZ optimized structure of F2F stacked uracil dimer in COSMO water solution.

O	2.30981900	0.27668300	-1.85137600
C	1.98585800	0.13448000	-0.68956800
N	1.95924800	1.18705600	0.21124000
H	2.13694300	2.09873300	-0.19295100
N	1.59329100	-1.07289000	-0.14371000
H	1.51049900	-1.83653300	-0.81176800
C	1.43529400	1.08077700	1.47424100
H	1.40653200	2.00459500	2.04094500
C	0.98232200	-1.27314100	1.10298800
O	0.49280400	-2.35294600	1.38337600
C	0.97932700	-0.09121300	1.95860100
H	0.55817600	-0.17927400	2.95045700
O	-0.81735900	-1.56076300	-1.96528100
C	-1.24397200	-0.76234700	-1.15770700
N	-0.91482000	0.58246600	-1.16231100
H	-0.26739700	0.86619500	-1.89600600
N	-2.09553100	-1.11582500	-0.12520400
H	-2.25408100	-2.11146600	-0.02831900
C	-1.25192900	1.54555500	-0.20078800
O	-0.75654600	2.65840000	-0.24699800
C	-2.53700600	-0.23287800	0.82705000
H	-3.18373300	-0.65801200	1.58629300
C	-2.18419700	1.06758900	0.81338800
H	-2.52616700	1.76619400	1.56425400

Table S7 MP2/aug-cc-pVDZ optimized structure of F2F stacked uracil dimer in the gas phase.

O	1.5222661	0.9414386	-2.1373639
C	1.5789448	0.4731536	-1.0028672
N	1.8465990	1.2442683	0.1205915
H	1.9009999	2.2435246	-0.0483883
N	1.3653251	-0.8686003	-0.7104800
H	1.1003516	-1.4431853	-1.5110574
C	1.8077580	0.7539001	1.4059125
H	1.9975032	1.4844126	2.1929072
C	1.2389561	-1.4624268	0.5590096
O	0.8837126	-2.6406590	0.6661836
C	1.5393219	-0.5582236	1.6630190
H	1.5068652	-0.9430655	2.6800598
O	-1.3724837	-1.0319090	-2.1350228
C	-1.5028494	-0.5168241	-1.0274220
N	-1.2897409	0.8332754	-0.7744002
H	-0.9672825	1.3737672	-1.5777963
N	-1.8607650	-1.2366644	0.1046318
H	-1.9176068	-2.2414057	-0.0266028
C	-1.2671925	1.4826082	0.4736539
O	-0.9063631	2.6610458	0.5586747
C	-1.9315635	-0.6885532	1.3650213
H	-2.1962815	-1.3816347	2.1641610
C	-1.6752141	0.6325416	1.5859924
H	-1.7276291	1.0629769	2.5837330

Table S8 MP2/aug-cc-pVDZ optimized structure of F2F stacked uracil dimer in COSMO water solution.

O	1.7090425	0.3852110	-2.2892026
C	1.6466742	0.2160268	-1.0652085
N	1.9285434	1.2050696	-0.1473600
H	2.2240988	2.1002197	-0.5267002
N	1.2726405	-0.9873681	-0.4899829
H	1.0842832	-1.7473308	-1.1433210
C	1.8760486	1.0160814	1.2136610
H	2.1406137	1.8832672	1.8180200
C	1.1832646	-1.2904311	0.8757335
O	0.8434811	-2.4302994	1.2332409
C	1.5084907	-0.1827972	1.7538296
H	1.4671580	-0.3255884	2.8318081
O	-1.6082369	-0.4835800	-2.3528580
C	-1.6054459	-0.2618519	-1.1357123
N	-1.2585397	0.9655317	-0.5951835
H	-1.0378043	1.6969152	-1.2706172
N	-1.9328537	-1.2107689	-0.1909661
H	-2.2107738	-2.1216405	-0.5453879
C	-1.2356659	1.3272260	0.7589644
O	-0.9125280	2.4817627	1.0832082
C	-1.9467254	-0.9632743	1.1615838
H	-2.2416266	-1.8038512	1.7890505
C	-1.6046080	0.2580774	1.6669929
H	-1.6158994	0.4471547	2.7385579

Table S9 MP2/cc-pVDZ optimized structure of F2B stacked uracil dimer in the gas phase.

O	1.3324359	-2.4973631	0.1073575
C	1.5466342	-1.2940283	0.1614996
N	2.2962016	-0.6166766	-0.7939951
H	2.6601252	-1.1940242	-1.5441854
N	1.0820451	-0.4617946	1.1660946
H	0.5011678	-0.9134507	1.8753000
C	2.4367063	0.7536313	-0.8213911
H	3.0098663	1.1526645	-1.6612266
C	1.1324152	0.9494794	1.2329001
O	0.5719323	1.5496028	2.1396930
C	1.8901645	1.5496346	0.1363791
H	1.9866771	2.6336224	0.1006389
O	-1.9222042	-1.0985386	1.7971336
C	-1.7729636	-0.6782499	0.6592859
N	-1.5270936	-1.5150458	-0.4262400
H	-1.3301187	-2.4804608	-0.1764269
N	-1.8245548	0.6626872	0.3124188
H	-1.9264211	1.3009798	1.1023286
C	-1.1620554	-1.0441663	-1.6671222
H	-0.9137233	-1.8119825	-2.4037844
C	-1.4525529	1.2632517	-0.9097944
O	-1.4131870	2.4800347	-1.0265796
C	-1.1335691	0.2859501	-1.9526349
H	-0.8653027	0.6513148	-2.9431830

Table S10 MP2/cc-pVDZ optimized structure of F2B stacked uracil dimer in COSMO water solution.

O	1.5632119	-2.5671580	0.5616761
C	1.6262139	-1.3516566	0.4089490
N	2.1451665	-0.7489685	-0.7215021
H	2.5043062	-1.3729140	-1.4398112
N	1.1804087	-0.4414312	1.3543487
H	0.7584500	-0.8525422	2.1878405
C	2.1947574	0.6115709	-0.9011198
H	2.6286041	0.9431833	-1.8468712
C	1.1584504	0.9594678	1.2750572
O	0.6840092	1.6259101	2.1951564
C	1.7272233	1.4784812	0.0400657
H	1.7604741	2.5555731	-0.1187568
O	-1.8926882	-1.2043134	1.6536830
C	-1.6762370	-0.7085537	0.5520338
N	-1.3402774	-1.4516986	-0.5638639
H	-1.2685165	-2.4571025	-0.4289242
N	-1.7376266	0.6519972	0.3036561
H	-1.9419424	1.2332821	1.1169932
C	-1.0694319	-0.8960248	-1.7918761
H	-0.8173176	-1.6066282	-2.5820320
C	-1.4565339	1.3345450	-0.8902084
O	-1.5113230	2.5629802	-0.9304224
C	-1.1192004	0.4497406	-1.9965054
H	-0.8975557	0.8793323	-2.9731004

Table S11 MP2/aug-cc-pVDZ optimized structure of F2B stacked uracil dimer in the gas phase.

O	1.6568229	-2.3591977	-0.2069465
C	1.6825830	-1.1296041	-0.1309160
N	2.1883988	-0.3224162	-1.1415976
H	2.5611481	-0.8185572	-1.9427220
N	1.2106256	-0.4127883	0.9546718
H	0.8323572	-0.9681157	1.7237037
C	2.1078639	1.0553865	-1.1293987
H	2.4952311	1.5587127	-2.0158706
C	1.0865883	0.9894537	1.0842105
O	0.5938545	1.4741197	2.1028122
C	1.5667134	1.7308249	-0.0766697
H	1.4824249	2.8154570	-0.0765715
O	-1.6551351	-1.3847616	1.9107631
C	-1.6093465	-0.8908435	0.7853052
N	-1.3378740	-1.6422179	-0.3531038
H	-1.0752246	-2.6066602	-0.1739279
N	-1.8045350	0.4565801	0.5251666
H	-1.9395888	1.0389793	1.3512788
C	-1.0961337	-1.0777362	-1.5861889
H	-0.8215228	-1.7789401	-2.3753904
C	-1.5663452	1.1438756	-0.6822612
O	-1.6599282	2.3711368	-0.7332084
C	-1.2050393	0.2662715	-1.7929035
H	-1.0325746	0.7082626	-2.7723392

Table S12 MP2/aug-cc-pVDZ optimized structure of F2B stacked uracil dimer in COSMO water solution.

O	1.9802103	-2.1877042	-0.0543050
C	1.8313013	-0.9592944	-0.0203154
N	2.3181501	-0.1057367	-0.9866031
H	2.8445643	-0.5334690	-1.7437897
N	1.1488292	-0.3144282	0.9974641
H	0.8246501	-0.9127158	1.7574381
C	2.1414184	1.2568226	-0.9538212
H	2.5820696	1.8063043	-1.7857408
C	0.9215089	1.0619743	1.1401151
O	0.3092697	1.4844494	2.1341133
C	1.4481052	1.8651728	0.0531034
H	1.3107250	2.9444666	0.0704772
O	-2.0193357	-1.7763174	1.5796100
C	-1.7373886	-1.1431538	0.5524787
N	-1.1676816	-1.7236155	-0.5599873
H	-0.9915157	-2.7230992	-0.5086360
N	-1.9598056	0.2150821	0.4230891
H	-2.3808886	0.6723506	1.2308180
C	-0.7842353	-1.0105237	-1.6718067
H	-0.3320445	-1.5962504	-2.4726389
C	-1.6112423	1.0392283	-0.6540623
O	-1.8591503	2.2551428	-0.6072726
C	-0.9685458	0.3404291	-1.7518243
H	-0.6648486	0.8982036	-2.6356898

Table S13 S_1/S_0 CI geometry of F2F10W deactivating via a monomer like Eth-CoI mechanism.

C	-2.2132936	-1.6395989	1.3260981
C	-2.1572277	0.1884536	-0.3743430
C	-2.2276124	1.1240298	0.6749189
C	-2.2401950	0.6350050	1.9253379
H	-2.5181746	-1.7330588	-0.7362928
H	-2.0773340	-0.9903398	3.2911007
H	-2.1448972	1.3222946	2.7438689
H	-2.1467675	2.2228326	0.5482487
N	-2.3912818	-1.1113930	0.0451274
N	-2.2115983	-0.6833697	2.3191811
O	-2.1744390	-2.8501913	1.6352633
O	-1.9841990	0.4232333	-1.5723932
C	1.5439698	-0.5682556	-1.8078994
C	0.7973302	-0.6083866	0.5160886
C	1.0732296	0.8539275	0.5025626
C	0.8503506	1.5042684	-0.8914012
H	0.6310935	-2.1735092	-0.8163559
H	1.8265965	1.2529656	-2.7769400
H	0.6811054	2.6035536	-1.0371458
H	2.0452535	1.0258078	1.0330389
N	0.6700921	-1.1389569	-0.8218669
N	1.7140699	0.8032155	-1.8473039
O	1.9002259	-1.1636087	-2.8632653
O	0.8044666	-1.3649067	1.4602393
H	0.8913535	-0.4462417	-4.9397057
H	2.2843907	-0.7242626	-4.8728394
O	1.6680901	-0.3906881	-5.5889571

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H	-1.5549020	-4.1745868	0.1714526
H	-2.2497794	-5.4484191	0.0146419
O	-1.7026169	-4.8305450	-0.4591117
H	-3.5575923	-3.2488054	-2.1017317
H	-2.3233992	-3.8500454	-1.4620455
O	-2.6188828	-3.0358049	-1.9346258
H	-1.7832156	2.3787533	-2.3663945
H	-1.4637489	2.5532590	-3.7405009
O	-1.2894811	3.0448424	-2.8999166
H	2.8056450	2.4797696	-4.5394858
H	1.9146737	1.2438969	-4.8640807
O	2.0512645	1.8915695	-4.1551765
H	-0.0632389	-3.6759133	2.2915602
H	0.7977129	-2.5487803	2.9477207
O	0.4439309	-3.4383615	3.0891627
H	-4.7799406	-4.1631785	0.5573602
H	-3.5568251	-4.0518177	1.4775810
O	-4.2645939	-4.6872269	1.1987557
H	-1.2738502	-2.6386610	4.4475967
H	-2.7016492	-2.7685132	3.9212853
O	-2.1472984	-2.2305386	4.5096001
H	5.0351842	-2.4856106	-2.7783802
H	4.9148326	-1.0503337	-2.4646105
O	4.6625731	-1.6691369	-3.1732665
H	0.7958881	-3.3466641	-2.7449983
H	0.2613414	-4.5257832	-1.9724666
O	1.1140383	-4.1906300	-2.2876121

Table S14 S_1/S_0 CI geometry of F2F10W deactivating via a dimerization like CoI mechanism.

C	-2.1642568	-1.7651746	1.1251878
C	-1.8200338	0.3141215	-0.0592440
C	-1.3081174	1.0277816	1.1325610
C	-1.1917108	0.2186759	2.3037188
H	-2.6061918	-1.2971535	-0.7980695
H	-1.6245187	-1.4337326	3.1652897
H	-1.0953241	0.8014249	3.2264545
H	-1.3407315	2.1865171	1.0894210
N	-2.4688073	-0.9102440	0.1242520
N	-1.8124889	-1.0259620	2.2581662
O	-2.4653716	-2.9693786	1.1520510
O	-1.7430710	0.8535771	-1.1779205
C	0.7826377	-0.5906785	-0.9504080
C	0.8539772	-1.3171789	1.4963029
C	1.1813033	0.0993841	1.7996165
C	0.8549506	1.0900370	0.6905944
H	0.1622122	-2.3668869	-0.2569353
H	1.0290352	1.3961392	-1.3126881
H	1.3155670	2.0777917	0.8461000
H	1.8434102	0.2069400	2.6151164
N	0.5281669	-1.4752388	0.1303982
N	1.1661371	0.6570411	-0.5436661
O	0.6758233	-1.0409121	-2.0953458
O	0.9112052	-2.2247607	2.2923433
H	-1.7843110	-5.0537543	0.7115484
H	-0.3946538	-5.5826639	0.5740328
O	-1.2758323	-5.6497412	0.1584780

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H	-1.4229950	-2.3302578	-2.3148022
H	-2.1003850	-1.1233242	-2.9924210
O	-2.3343125	-1.9216373	-2.5789676
H	-2.4532977	3.0363713	-0.2577812
H	-3.2872845	3.2281748	1.0233797
O	-2.6908506	3.6853722	0.4619189
H	0.6052440	0.9767682	-3.2827846
H	0.2503442	2.2976120	-3.5055288
O	0.9758216	1.8182924	-3.1924642
H	0.3431225	-4.0451302	4.4166397
H	0.7554210	-2.6531594	3.9733411
O	0.9085037	-3.2526177	4.7141084
H	1.5869899	-4.3050602	2.6304249
H	2.0079896	-4.7706657	1.4171925
O	1.3720610	-5.0210304	2.0237992
H	-0.4951066	-2.1572696	5.3065444
H	-1.8542344	-1.7893161	5.7312852
O	-1.1345576	-1.5093988	5.1263899
H	1.0550236	-2.2771463	-3.4343950
H	1.5405928	-2.1857868	-4.9186264
O	1.6278764	-2.7309172	-4.1000071
H	-4.3222876	-0.4827165	-2.7590870
H	-3.1966757	0.5328719	-2.4947560
O	-4.0694802	0.4061308	-2.9609259
H	0.2800456	-3.6964068	-1.9105271
H	-0.9777891	-4.3386494	-1.2091651
O	-0.6514353	-3.5911638	-1.7325116

Table S15 S_1/S_0 CI geometry of F2F10W deactivating via a dimerization like CoI mechanism.

C	-3.3133009	-2.2311215	1.4428792
C	-2.8970501	-0.4707287	-0.3266730
C	-2.5805761	0.4834803	0.7287296
C	-2.4165253	-0.0574787	2.0941749
H	-3.2793742	-2.4118920	-0.6812703
H	-2.8974261	-1.5299688	3.4536428
H	-1.9684738	0.5720522	2.8641587
H	-2.2255065	1.5496253	0.5997408
N	-3.1372353	-1.7561249	0.1525648
N	-3.0939169	-1.1948549	2.4199047
O	-3.7053784	-3.3972296	1.6806170
O	-3.0546227	-0.1432258	-1.5777330
C	-0.5588874	-1.7236340	-1.8826706
C	-0.2320272	-2.2312095	0.6175509
C	-0.1878897	-0.8307469	0.8470736
C	-0.5748810	0.1379351	-0.2629208
H	-0.9080674	-3.4991504	-0.9150301
H	-0.2594509	0.2794057	-2.3141006
H	-0.0006543	1.0631319	-0.1014416
H	0.6169667	-0.5655924	1.5532521
N	-0.4874611	-2.5601393	-0.7607222
N	-0.2341874	-0.4094249	-1.5542586
O	-0.8185037	-2.0590401	-3.0531664
O	-0.1322290	-3.1165907	1.4260072
H	-0.9664364	0.4117739	-5.3667837
H	-0.4172478	-0.7389431	-4.4510545
O	-0.2449187	0.1392682	-4.8351128

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H	-2.3570104	-5.9519409	0.9412132
H	-1.1616428	-5.0046062	1.0785821
O	-1.3862922	-5.9437553	0.8041108
H	-3.2771232	-3.2077346	-2.5299040
H	-2.9971262	-4.3293611	-1.6064223
O	-3.7070642	-3.6109251	-1.7602522
H	-2.1209556	2.1130289	-1.4938599
H	-1.3591611	3.4184392	-1.8621129
O	-1.5953878	2.8230997	-1.0697241
H	1.5884647	2.4618140	-3.1563284
H	0.5366390	1.6178459	-3.9154584
O	0.6755678	2.2957065	-3.2098550
H	-2.6428323	-3.9911233	3.4229513
H	-1.1192772	-3.7879232	3.4485391
O	-1.8781113	-3.7864802	4.0468096
H	-6.5091769	-5.5854017	1.6602881
H	-5.1698306	-6.0722074	2.1817954
O	-6.1028241	-6.1152108	2.3983198
H	-1.9536295	-2.2346956	4.8763181
H	-3.1028234	-1.6812522	5.7646601
O	-2.5463027	-1.4468775	5.0261299
H	-0.2172382	-3.6851968	-3.2392599
H	1.2512869	-4.1001258	-2.8351699
O	0.4692616	-4.4438847	-3.3360913
H	-1.0041915	-5.4114238	-2.5755398
H	-1.3401946	-5.7737429	-1.0574537
O	-1.5399279	-5.1893373	-1.7686702

Table S16 S_1/S_0 CI geometry of F2B10W deactivating via a monomer like Eth-CoIn mechanism.

C	4.5377173	7.2559957	5.6066935
C	7.2532456	8.3121326	8.4593299
C	7.2595470	6.8362783	8.4233366
C	5.8279332	6.9197812	4.6503049
C	4.4565003	6.2982239	6.6276992
C	5.5191640	4.6243986	5.2010251
C	8.4431593	7.1162845	6.2150375
C	7.9396719	9.0841425	7.5045403
H	8.0438326	5.3449372	7.1160682
H	6.3460905	5.2673647	3.4855245
H	6.6547380	8.7210759	9.3010398
H	3.5166418	7.5572882	5.2708555
H	8.0417579	10.1829330	7.5440255
H	8.8703849	9.1475612	5.6755445
H	5.0175668	4.3629081	7.1922956
H	6.7241384	7.4868980	4.3898534
N	7.8680202	6.3407647	7.2237080
N	5.7406408	5.5943605	4.2827811
N	5.2436580	5.1084211	6.5049230
N	8.5629358	8.4569375	6.4189828
O	6.7755932	6.0968002	9.3026530
O	3.5613643	6.2328719	7.5444053
O	5.6893678	3.4417024	4.9583146
O	8.7871679	6.5491142	5.1374540
H	10.8523991	7.7411522	3.9172584
H	9.7087311	7.4654158	3.0294461
O	10.4231861	8.1226301	3.1241652

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H	8.6313970	5.0908286	3.4452481
H	8.3292353	4.1683668	2.2024327
O	8.0745565	5.0938583	2.5806905
H	3.4351224	7.2641310	9.2603855
H	2.9628089	7.3450409	10.7057646
O	3.6669783	7.7229497	10.1266746
H	3.5498207	5.1244140	9.6748944
H	4.8300213	4.9410149	10.2202429
O	3.9695395	4.4477598	10.2019870
H	2.3618478	4.8325011	7.5472229
H	1.0164190	5.0406715	7.7565656
O	1.5860433	4.2856146	7.5861305
H	9.7203765	9.5195867	3.8344354
H	9.3306586	10.9976686	3.8960777
O	9.3522262	10.1294568	4.4404081
H	9.6369716	3.6204645	7.3275139
H	8.3331845	3.0413518	6.8929692
O	8.9716287	3.6759232	6.5383615
H	3.7643858	2.4031575	8.0938750
H	5.0732334	2.5063862	7.0940382
O	4.1130553	2.5917151	7.1303978
H	5.9406463	2.7642135	8.6400144
H	6.7231470	4.0893583	8.6652786
O	6.8354732	3.1246035	8.5491876
H	4.6864713	2.5089430	2.9589199
H	4.7322547	1.0571992	3.0330053
O	5.1397228	1.7750006	2.4984510

Table S17 S_1/S_0 CI geometry of F2B10W deactivating via a monomer like Eth-CoIn mechanism.

C	4.8908231	7.2728339	5.5946864
C	7.5173132	7.6690320	8.9993851
C	7.6524700	6.2932226	8.4265961
C	6.0561237	7.1506122	4.7623930
C	4.4663934	6.1165752	6.3665598
C	5.8204888	4.8096811	4.7436439
C	8.5251542	7.2915015	6.2406780
C	7.9316564	8.7146775	8.1838273
H	8.3281882	5.2910582	6.7046235
H	6.5700148	5.8939701	3.1245949
H	7.1766062	7.7464040	10.0380055
H	4.1454198	7.4499631	4.8339411
H	7.9224175	9.7251784	8.5397204
H	8.8028560	9.3546986	6.3653774
H	5.2101506	4.1213827	6.5382448
H	6.5985475	8.0345413	4.3035277
N	8.1644628	6.2098678	7.1032640
N	5.9325784	5.9487142	3.9597855
N	5.3651428	5.0328534	6.0237850
N	8.4149318	8.5741773	6.9038633
O	7.4363850	5.2543164	9.0477804
O	3.7145744	6.0326726	7.3144775
O	6.1019552	3.6463707	4.3172748
O	8.9393759	7.1687186	5.0834771
H	8.2330574	5.2217077	2.0942042
H	7.4028700	4.1842421	2.7627928
O	7.4086093	4.8127099	2.0534752

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H	3.2269571	7.4364286	9.5297120
H	3.7478528	6.9238911	10.7929821
O	3.1272710	7.5563215	10.4568426
H	10.6330824	9.3739012	9.4506558
H	11.0718461	10.2070746	8.4734165
O	10.3212450	10.1835090	9.0443858
H	1.3812023	5.2662098	7.6150508
H	0.8691058	6.5607244	7.2568545
O	0.6191858	5.6150278	7.1542381
H	11.1423337	7.1544691	2.8784631
H	12.1451065	6.4324620	3.7739738
O	11.2043500	6.4793658	3.5483279
H	9.0842944	10.2775757	4.2446693
H	9.8658965	11.3704962	4.6126858
O	9.3650736	10.6696081	5.0315942
H	9.5068853	3.4619365	6.2390610
H	8.0868527	3.1411116	6.2016297
O	8.6813945	3.8087522	6.0305097
H	3.1188977	3.4970272	5.7703549
H	3.5567159	2.1159402	6.0090210
O	3.3970491	2.9281505	6.4589272
H	5.6992614	2.4862497	8.2460085
H	6.8062777	3.4380558	8.5042305
O	6.6589814	2.5801750	8.1693398
H	4.5963013	2.5148137	2.8221037
H	3.3247972	3.2575621	2.4227582
O	3.8191590	2.4044164	2.3444798

Table S18 S_1/S_0 CI geometry of F2B10W deactivating via a monomer like CO-CoIn mechanism.

C	3.2168296	6.6607032	5.7079855
C	6.2510226	8.2157304	7.2256357
C	6.7193468	6.9851626	7.8256035
C	4.1289348	6.5494679	4.3777585
C	3.3657672	5.6529122	6.5240377
C	5.2887491	4.6877364	5.5330641
C	8.4641998	6.8759925	6.0505695
C	6.9246781	8.6953732	6.1414558
H	8.0549794	5.4548165	7.5129201
H	5.9806916	5.6948272	3.8757443
H	5.4178033	8.7153533	7.7322128
H	2.5437671	7.4015729	6.1851096
H	6.5737597	9.5849511	5.6303833
H	8.2786610	8.3781114	4.5754445
H	4.5020340	4.0054720	7.4103923
H	4.0647883	7.2237380	3.5065074
N	7.8287092	6.4555336	7.2030504
N	5.2742631	5.7639774	4.6226827
N	4.2325932	4.5326923	6.5298390
N	8.0410335	8.1101833	5.5842107
O	6.1384517	6.3730031	8.7113437
O	2.8461265	5.6881036	7.8734697
O	6.1834521	3.8151511	5.6171604
O	9.2530608	6.1743802	5.3973488
H	10.1179829	6.2887442	3.2700094
H	9.7049605	6.3692552	1.7926328
O	10.1797716	6.8485693	2.4873371

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H	7.9695079	5.3866493	3.4967502
H	7.1928414	4.4241534	2.5508118
O	7.6556188	5.3156603	2.5700733
H	3.8309907	5.7896245	10.3824447
H	3.6520993	6.6426340	11.5808261
O	3.7677339	5.7374966	11.3567971
H	1.7837473	2.6557578	12.4531623
H	1.6629632	4.0097567	12.0010103
O	1.6209079	3.1304058	11.6561908
H	9.1352230	8.3290178	2.8034400
H	7.7589389	7.9429732	2.5946794
O	8.2451034	8.6139282	3.0687013
H	8.1481371	3.0073190	8.3976540
H	6.9172639	3.4288430	7.4664386
O	7.7785479	3.7422047	7.8950924
H	3.0118212	2.6547914	9.3000278
H	4.1754674	3.2756647	10.0453805
O	3.8089432	3.1769578	9.1225886
H	8.1499220	3.3759334	5.6001766
H	9.1590529	3.5774647	4.4030999
O	8.3909722	3.0438937	4.7248397
H	6.5270518	4.1177139	9.7289067
H	5.7946477	4.6017809	10.9927885
O	6.0084774	3.8084005	10.5178594
H	5.6086493	2.3812283	2.7947485
H	6.9937459	2.3100535	3.3229829
O	6.5281535	2.5126927	2.5076200

Table S19 Structure of the cyclobutane uracil dimer at the end of the simulation time in the representative trajectory displayed in Figure 6.

C	-2.159910	-1.762140	1.124150
C	-1.820610	0.317314	-0.060789
C	-1.314620	1.027600	1.131140
C	-1.194530	0.225847	2.302440
H	-2.604620	-1.316440	-0.807532
H	-1.608500	-1.433420	3.174540
H	-1.107310	0.786218	3.213060
H	-1.334620	2.165990	1.068470
N	-2.471160	-0.910838	0.121153
N	-1.811850	-1.024000	2.258580
O	-2.464140	-2.973580	1.152990
O	-1.742000	0.853266	-1.179580
C	0.781876	-0.590953	-0.954661
C	0.846928	-1.307200	1.494900
C	1.187820	0.097871	1.797940
C	0.864358	1.088720	0.692348
H	0.167106	-2.368760	-0.245338
H	1.027710	1.408610	-1.309960
H	1.334030	2.061810	0.857455
H	1.838920	0.210613	2.614290
N	0.527490	-1.472360	0.130945
N	1.164140	0.653448	-0.544301
O	0.672844	-1.040910	-2.095580
O	0.907819	-2.225490	2.291800
H	-1.786030	-5.040580	0.718634
H	-0.374434	-5.587030	0.578638
O	-1.276350	-5.650310	0.159644

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H	-1.423950	-2.317400	-2.312850
H	-2.101980	-1.117230	-2.989880
O	-2.337530	-1.922530	-2.579100
H	-2.454720	3.042610	-0.253274
H	-3.299370	3.232920	1.015700
O	-2.692600	3.687330	0.455114
H	0.597886	0.973909	-3.270860
H	0.248094	2.295320	-3.508040
O	0.981416	1.824540	-3.192110
H	0.342015	-4.039820	4.409890
H	0.755150	-2.672200	3.970780
O	0.910474	-3.254290	4.715950
H	1.586270	-4.304900	2.644170
H	2.010320	-4.764130	1.393280
O	1.371120	-5.024450	2.019270
H	-0.496033	-2.159290	5.307780
H	-1.861030	-1.795450	5.727650
O	-1.133330	-1.508850	5.124090
H	1.050880	-2.277140	-3.444800
H	1.535200	-2.180880	-4.951020
O	1.633340	-2.730330	-4.097810
H	-4.336810	-0.474310	-2.760710
H	-3.201440	0.518922	-2.484540
O	-4.071140	0.405534	-2.960370
H	0.279927	-3.717000	-1.920030
H	-0.979919	-4.325600	-1.206330
O	-0.654895	-3.590720	-1.731750