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

SUPPORTING INFORMATION FOR:

Triplet photosensitization mechanism of thymine by an oxidized nucleobase: from a dimeric model to DNA environment

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Table S1. CASSCF(18,13)/CASPT2 vertical absorption energies, oscillator strengths (*f*) and nature of the five lowest-lying excited states of isolated ForU.

State	Energy (au)	Vertical Absorption Energy (eV)	*f*	Nature
S_0	-565.9792303	0.00		
S_1	-565.8529732	3.44	0.0000	n,π* (aldehyde)
S_2	-565.8369456	3.87	0.2961	π,π*
S_3	-565.8061073	4.71	0.0002	n,π* (ketone)
S_4	-565.7810417	5.39	0.0014	
S_5	-565.7759439	5.53	0.0007	

Table S2. CASSCF(14,13)/CASPT2 vertical absorption energies, oscillator strengths (*f*) and nature of the five lowest-lying excited states of the ForU-Thy dimer.

State	Energy (au)	Vertical Absorption Energy (eV)	*f*	Nature
S_0	-1058.146933	0.00	-	S_0
S_1	-1058.015869	3.57	0.0006	$^1n,\pi^*_{ForU}$
S_2	-1057.988751	4.30	0.2447	$^1\pi,\pi^*_{ForU}$
S_3	-1057.98426	4.43	0.3002	$^1\pi,\pi^*_{THY}$
S_4	-1057.951026	5.33	0.0128	^1CT
T_1	-1058.023314	3.36	-	$^3\pi,\pi^*_{ForU}$
T_2	-1058.021212	3.42	-	$^3n,\pi^*_{ForU}$
T_3	-1058.013557	3.63	-	$^3\pi,\pi^*_{THY}$
T_4	-1057.96745	4.88	-	^3CT

Table S3. TD-DFT vertical absorption energies, oscillator strengths (*f*) and nature of the five lowest-lying excited states of the ForU-Thy dimer.

State	Vertical Absorption Energy (eV)	*f*	Nature
S_0	0.00	-	S_0
S_1	3.88	0.0002	$^1n,\pi^*_{ForU}$
S_2	4.65	0.0300	^1CT
S_3	4.86	0.2541	$^1\pi,\pi^*_{ForU}$
S_4	5.08	0.0008	$^1n,\pi^*_{THY}$
S_5	5.14	0.0001	$^1n,\pi^*_{ForU}$
S_6	5.26	0.1589	$^1\pi,\pi^*_{THY}$
T_1	3.25	-	$^3\pi,\pi^*_{FoU}$
T_2	3.44	.	$^3n,\pi^*_{ForU}$
T_3	3.49	-	$^3\pi,\pi^*_{THY}$
T_4	4.63	-	^3CT
T_5	4.69	-	$^3n,\pi^*_{THY}$

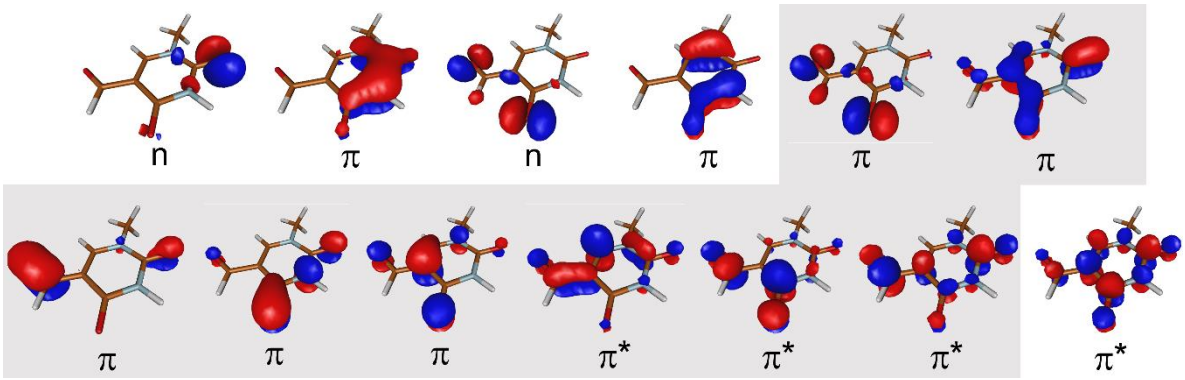

Figure S1. CASSCF(18,13) natural orbitals employed in the CASSCF/CASPT2 calculations on the ForU monomer. Molecular orbitals in the shaded box compose the CASSCF(10,8) active space.

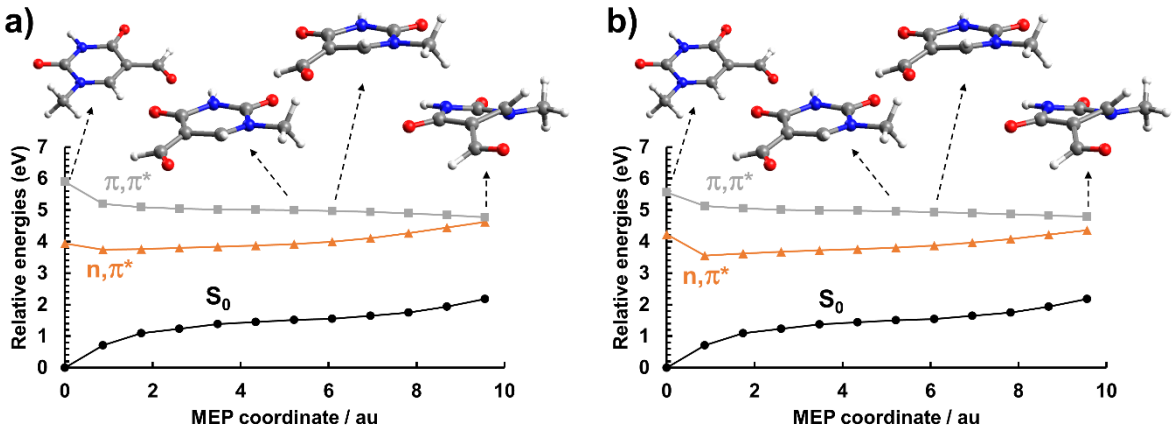

Figure S2. Minimum energy path calculation of the π,π* state of ForU computed with the CASSCF(10,8) method. Panel a) shows the CASSCF(10,8) energies and panel b) displays the CASSCF(18,13) energies.

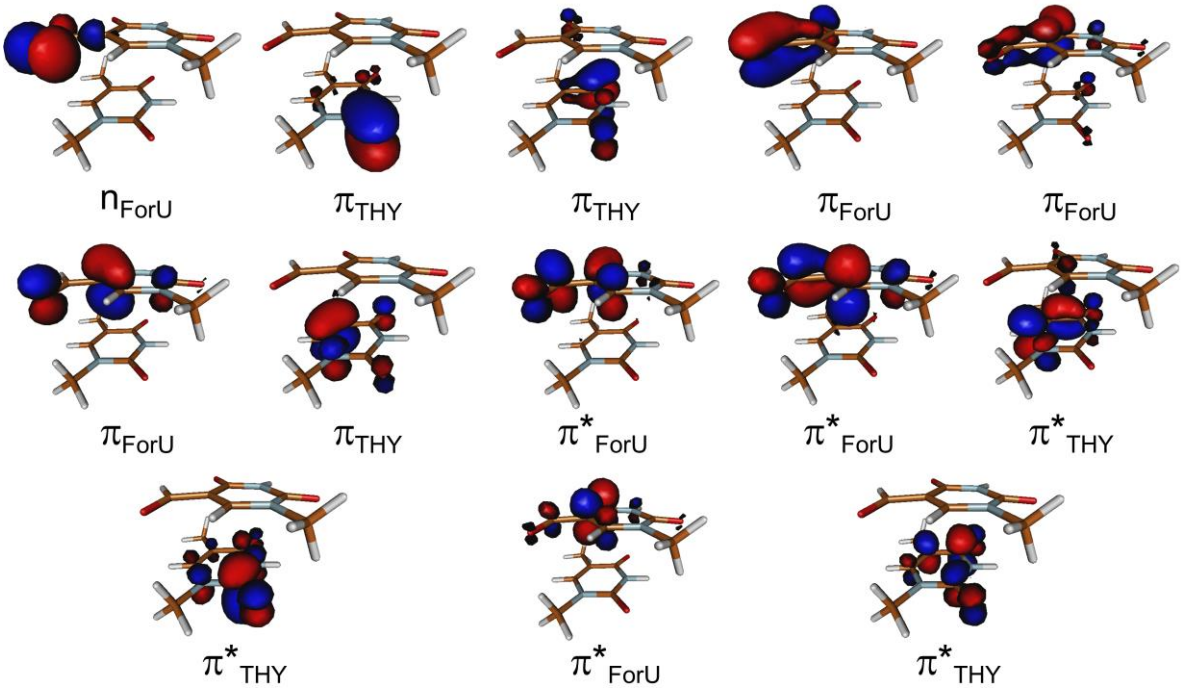

Figure S3. CASSCF(14,13) natural orbitals employed in the CASSCF/CASPT2 calculations on the ForU-Thy dimer.

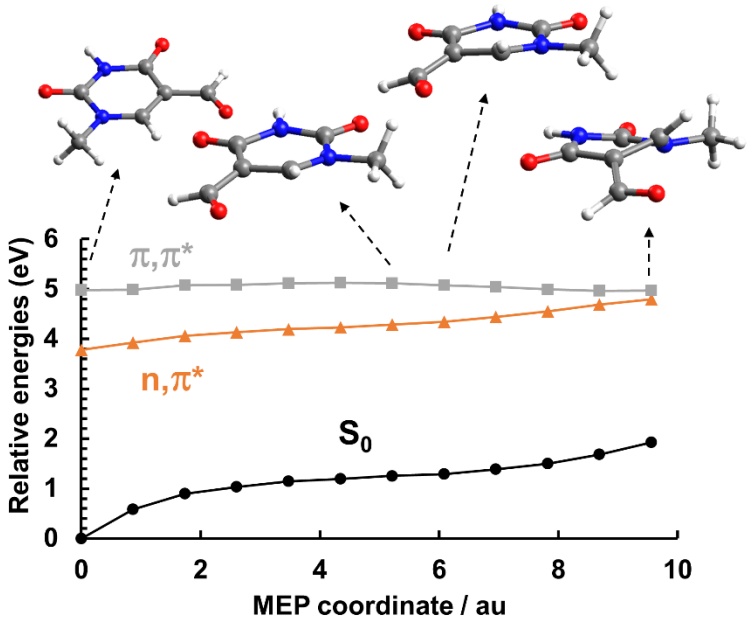

Figure S4. Minimum energy path calculation of the π,π* state of ForU computed with the CASSCF(10,8) method. Energies computed at the TD-DFT level.

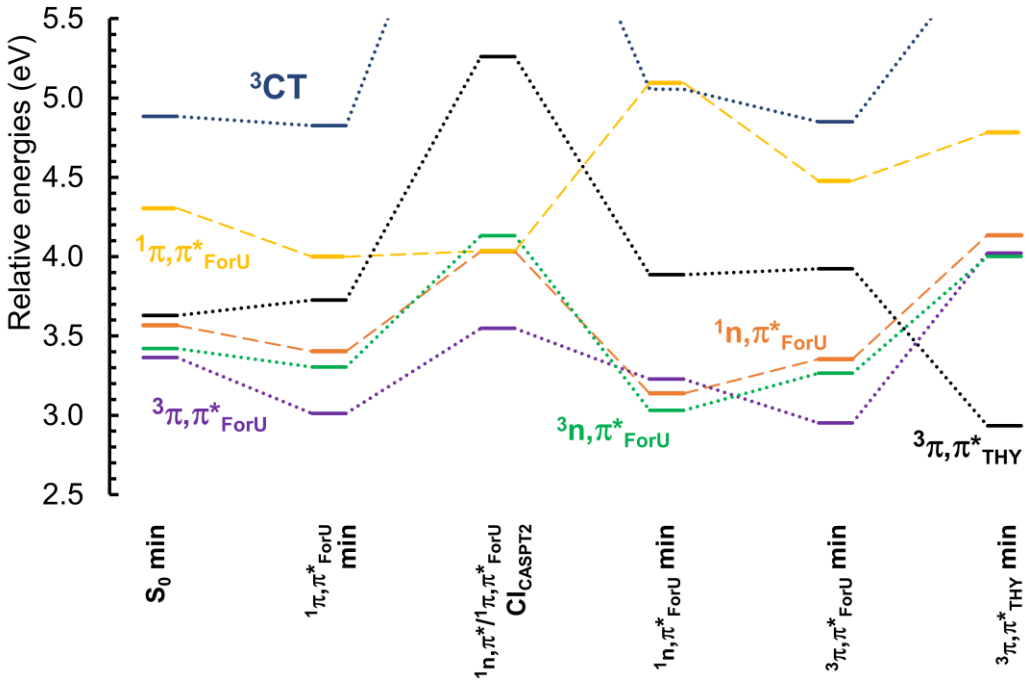

Figure S5. CASPT2 energy diagram of the triplet excited states (doted lines) of the ForU-Thy dimer at the relevant geometries for the thymine photosensitization process. Energies of the $^1n,\pi^*_{ForU}$ and $^1\pi,\pi^*_{ForU}$ singlet states (dashed lines) are also shown.

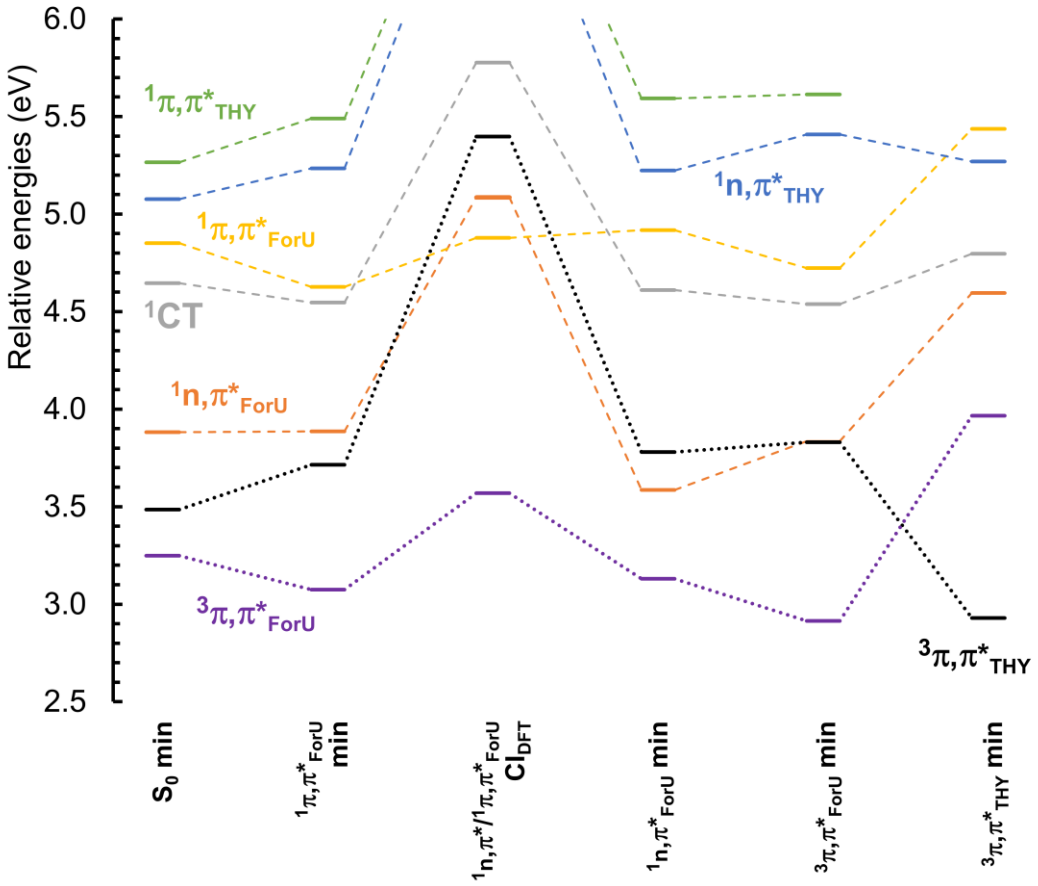

Figure S6. TD-DFT energy diagram of the singlet excited states (dashed lines) of the ForU-Thy dimer at the relevant geometries for the thymine photosensitization process. Energies of the $^3\pi,\pi^*_{ForU}$ and $^3\pi,\pi^*_{THY}$ triplet states (dotted lines) are also shown.

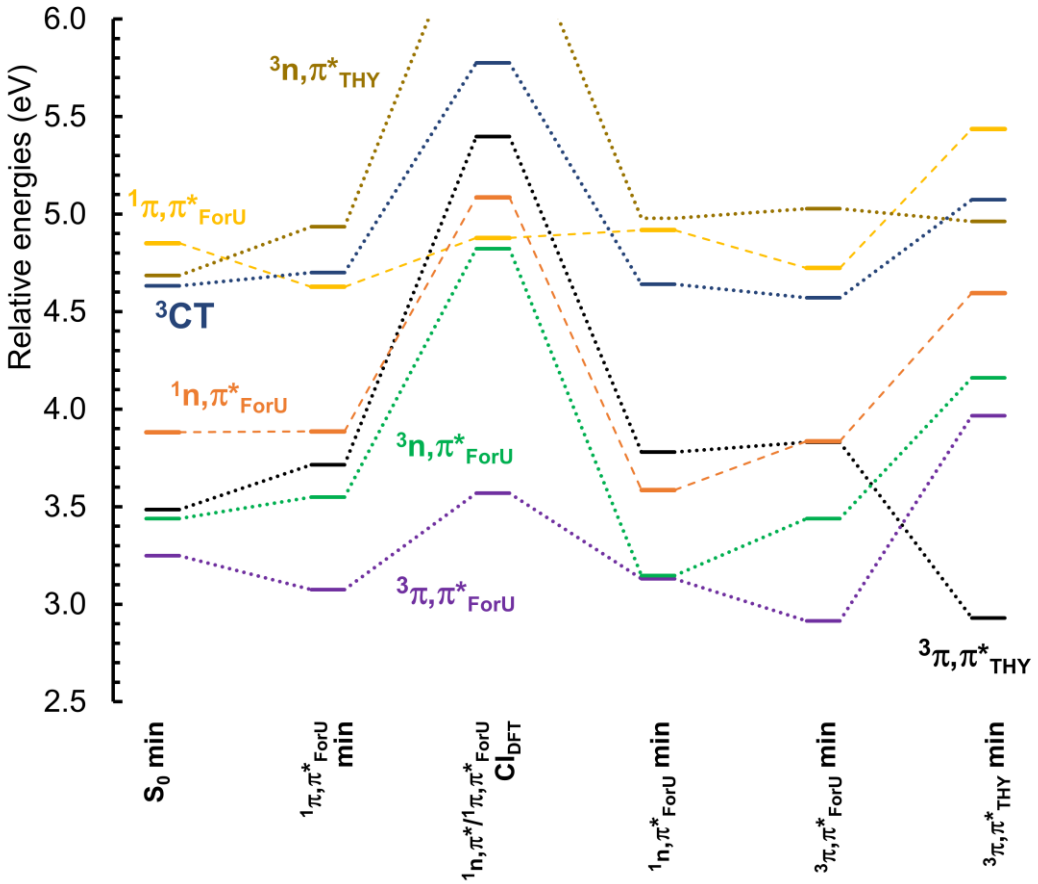

Figure S7. TD-DFT energy diagram of the triplet excited states (dotted lines) of the ForU-Thy dimer at the relevant geometries for the thymine photosensitization process. Energies of the ^{1}n,π*$_{ForU}$ and ^{1}π,π*$_{ForU}$ singlet states (dashed lines) are also shown.

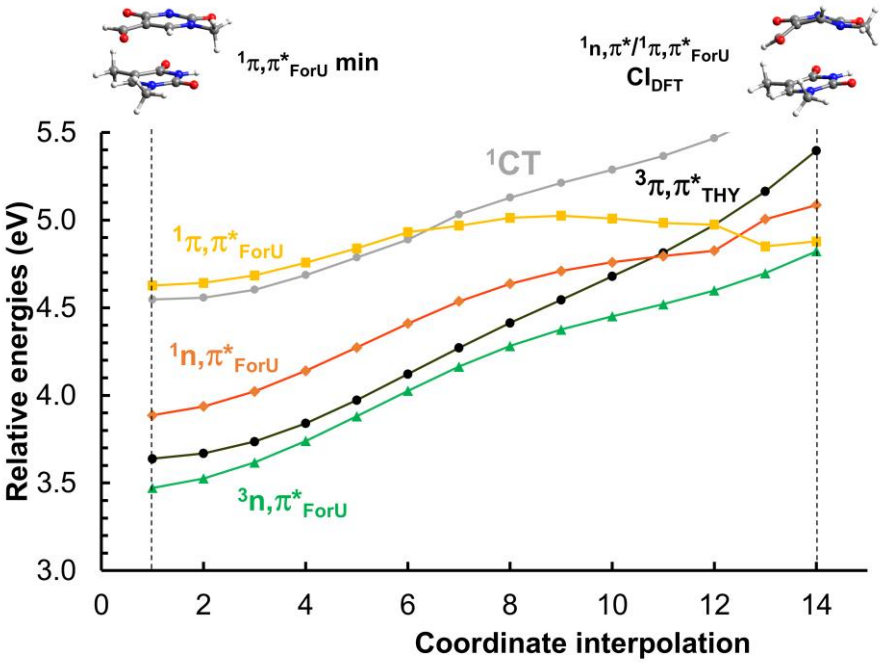

Figure S8. Coordinate interpolation between the $^1\pi,\pi^*_{ForU}$ min and the $^1n,\pi^*/^1\pi,\pi^*_{FoU}$ CI_{DFT} structures. Energies computed using the TD-DFT method.

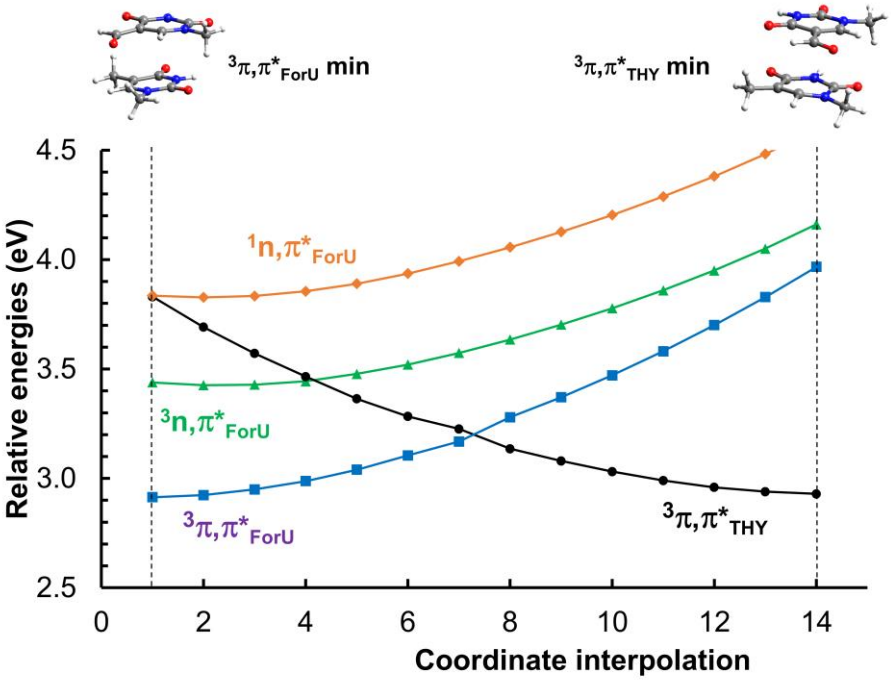

Figure S9. Coordinate interpolation between the $^3\pi,\pi^*_{ForU}$ min and the $^3\pi,\pi^*_{THY}$ min structures. Energies computed using the TD-DFT method.

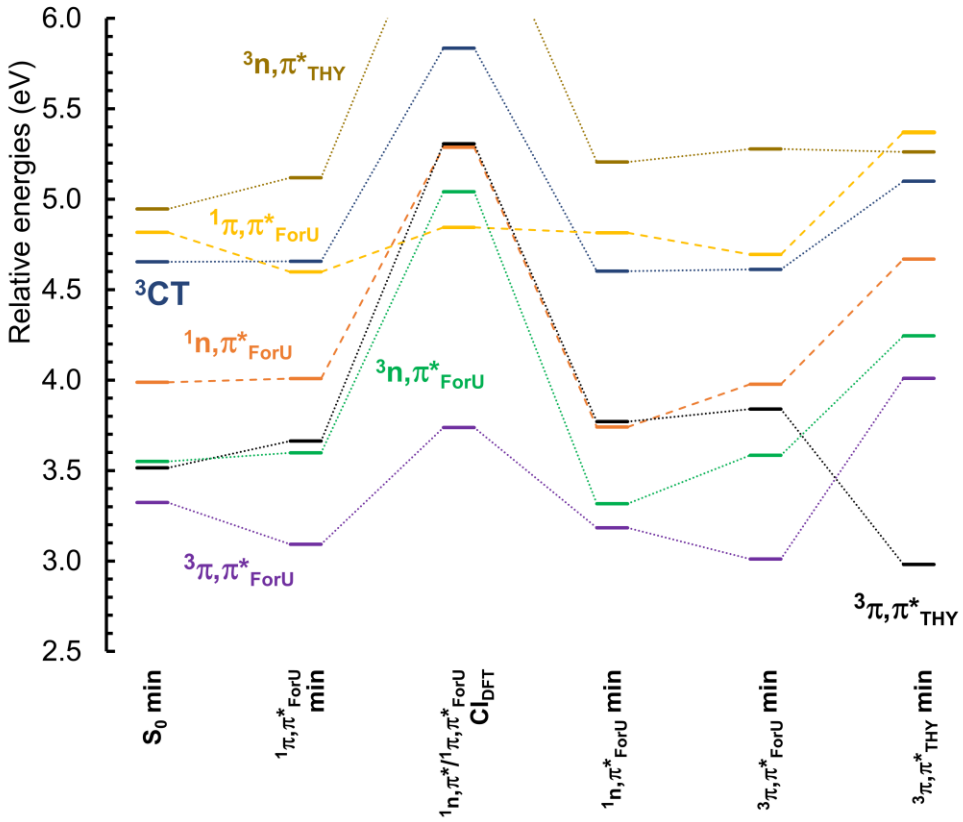

Figure S10. PCM-TD-DFT energy diagram of the triplet excited states (dotted lines) of the ForU-Thy dimer at the relevant geometries for the thymine photosensitization process. Energies of the ^{1}n,π*$_{ForU}$ and ^{1}π,π*$_{ForU}$ singlet states (dashed lines) are also shown.

Cartesian coordinates of the optimized structures of ForU-Thy with the TD-DFT method

S_0 min

H	-3.521536	-2.156879	4.377478
C	-3.640608	-3.132498	4.852077
N	-2.327776	-3.764410	4.972510
C	-2.229137	-5.125511	4.776005
O	-3.178985	-5.840428	4.485686
N	-0.957864	-5.634303	4.950377
C	0.193278	-4.954410	5.361690
O	1.242189	-5.559024	5.507370
C	-0.009261	-3.527668	5.604694
C	1.153503	-2.723090	6.097432
C	-1.241947	-3.021935	5.393769
H	-4.270683	-3.765224	4.229905
H	-1.458293	-1.972167	5.563223
H	1.495128	-3.113090	7.061033
H	0.878555	-1.672699	6.221507
H	1.992419	-2.788479	5.398925
H	-0.854780	-6.626727	4.773061
H	-3.431520	-7.972609	5.858256
C	-3.599939	-7.871438	6.931484
N	-2.615816	-6.951485	7.505672
C	-1.294726	-7.415854	7.602707
O	-0.980126	-8.529480	7.237549
N	-0.404479	-6.514288	8.142993
C	-0.643011	-5.184226	8.498346
O	0.256010	-4.484145	8.930591
C	-2.021662	-4.766596	8.272660
C	-2.412016	-3.373486	8.499081
C	-2.923822	-5.667916	7.793085
H	-3.508145	-8.842319	7.416905
H	-3.950572	-5.363810	7.612686
O	-3.504671	-2.918956	8.199730
H	0.561966	-6.819483	8.161559
H	-4.095504	-3.010103	5.839135
H	-4.593008	-7.457413	7.101626
H	-1.633071	-2.737660	8.951769

$^1\pi,\pi^*_{ForU}$ min

H	-3.534139	-2.360719	4.219471
C	-3.610383	-3.162688	4.958590
N	-2.317970	-3.832529	5.091673
C	-2.212871	-5.171637	4.781379
O	-3.153882	-5.866957	4.418820
N	-0.943554	-5.691161	4.936445
C	0.224520	-5.021823	5.324918
O	1.277390	-5.633608	5.411432
C	0.030267	-3.608542	5.624625
C	1.208524	-2.811139	6.091825
C	-1.217712	-3.105158	5.506836
H	-4.337197	-3.898533	4.620724
H	-1.433765	-2.065934	5.732753
H	1.596045	-3.221185	7.029223
H	0.932962	-1.766813	6.257408
H	2.016804	-2.851201	5.356263
H	-0.838228	-6.669091	4.691526
H	-3.714059	-7.577520	5.824258
C	-3.574759	-7.827802	6.882705
N	-2.618583	-6.891121	7.459933

C	-1.277977	-7.319111	7.563116
O	-0.923006	-8.422746	7.183385
N	-0.415809	-6.408529	8.141048
C	-0.708502	-5.090688	8.484297
O	0.180277	-4.357648	8.910861
C	-2.079545	-4.689756	8.275137
C	-2.500014	-3.318698	8.456274
C	-3.029486	-5.643273	7.791817
H	-3.178672	-8.835967	6.980517
H	-4.069766	-5.378072	7.650868
O	-3.669590	-2.988246	8.185851
H	0.560270	-6.681802	8.153619
H	-3.915979	-2.762905	5.930430
H	-4.523640	-7.720322	7.412851
H	-1.757877	-2.606883	8.841700

$^{1}n,\pi^{*}_{ForU}/^{1}\pi,\pi^{*}_{ForU}$ CI

H	-3.034172	-2.148272	4.279077
C	-3.246567	-3.093799	4.781407
N	-2.000619	-3.847004	4.924971
C	-2.031772	-5.214074	4.754079
O	-3.036631	-5.839246	4.443487
N	-0.822407	-5.841569	4.979684
C	0.381817	-5.269343	5.405131
O	1.358355	-5.973999	5.596256
C	0.319963	-3.822345	5.597500
C	1.544593	-3.122612	6.100650
C	-0.851882	-3.204448	5.343043
H	-3.932013	-3.682279	4.174661
H	-0.967189	-2.133632	5.476254
H	1.816922	-3.512799	7.086088
H	1.373699	-2.046330	6.183526
H	2.392820	-3.295480	5.432414
H	-0.809139	-6.840749	4.811543
H	-3.414708	-7.982748	5.894054
C	-3.714990	-7.647556	6.880895
N	-2.659397	-6.799922	7.445468
C	-1.396645	-7.427082	7.622626
O	-1.242690	-8.542106	7.243620
N	-0.449377	-6.717698	8.284546
C	-0.500190	-5.343882	8.608437
O	0.506740	-4.800185	8.981252
C	-1.786164	-4.749314	8.373211
C	-2.035977	-3.400216	8.257017
C	-2.956636	-5.628707	7.999959
H	-3.871616	-8.512425	7.519006
H	-3.967370	-5.440269	8.331163
O	-3.239430	-2.988315	8.128166
H	0.436412	-7.177262	8.382334
H	-3.685408	-2.902465	5.765347
H	-4.615763	-7.050058	6.814889
H	-1.216914	-2.683801	8.295310

$^{1}n,\pi^{*}_{ForU}$ min

H	-3.517837	-2.307591	4.156165
C	-3.579786	-3.123114	4.881147
N	-2.286030	-3.788592	4.992491
C	-2.203873	-5.144731	4.745571
O	-3.156650	-5.833039	4.408104
N	-0.942108	-5.675174	4.921634
C	0.221701	-5.016131	5.329708
O	1.263606	-5.635620	5.464806

C	0.045441	-3.588321	5.584754
C	1.226285	-2.803326	6.065262
C	-1.184680	-3.066351	5.407391
H	-4.307313	-3.855329	4.536591
H	-1.385139	-2.015928	5.593016
H	1.571368	-3.196383	7.026192
H	0.969838	-1.748461	6.191740
H	2.056532	-2.882551	5.357954
H	-0.856154	-6.669300	4.742921
H	-3.748312	-7.649335	5.854381
C	-3.580246	-7.891406	6.907126
N	-2.628490	-6.945051	7.487835
C	-1.303374	-7.321405	7.570080
O	-0.881133	-8.403379	7.202612
N	-0.453722	-6.363759	8.118452
C	-0.758025	-5.069525	8.484424
O	0.091298	-4.303867	8.911804
C	-2.173792	-4.720251	8.293789
C	-2.493497	-3.393766	8.606528
C	-3.050749	-5.672452	7.802983
H	-3.164247	-8.892903	6.996163
H	-4.099211	-5.472162	7.632104
O	-3.657085	-2.875599	8.471401
H	0.526524	-6.621099	8.120954
H	-3.885102	-2.731707	5.855432
H	-4.518688	-7.831122	7.461684
H	-1.687260	-2.751078	8.999382

$^{3}\pi,\pi^{*}_{ForU}$ min

H	-3.571936	-2.399737	4.097596
C	-3.637050	-3.191745	4.847922
N	-2.334008	-3.835558	5.003330
C	-2.207943	-5.180993	4.723106
O	-3.128184	-5.886609	4.336050
N	-0.939340	-5.685819	4.933087
C	0.202106	-5.003501	5.366125
O	1.255244	-5.601135	5.515033
C	-0.014932	-3.583588	5.630069
C	1.136634	-2.770843	6.135874
C	-1.256415	-3.090592	5.436667
H	-4.346636	-3.945672	4.513453
H	-1.487725	-2.048529	5.633084
H	1.485218	-3.165207	7.095333
H	0.847978	-1.725679	6.272012
H	1.977638	-2.816615	5.438384
H	-0.821429	-6.669413	4.718961
H	-3.865703	-7.439011	5.888157
C	-3.606096	-7.802281	6.886022
N	-2.618964	-6.899883	7.477115
C	-1.308515	-7.348452	7.599760
O	-0.946797	-8.446798	7.223338
N	-0.417601	-6.463531	8.197758
C	-0.649871	-5.148313	8.556600
O	0.234699	-4.446444	9.016465
C	-2.023684	-4.683832	8.313327
C	-2.337711	-3.305317	8.473557
C	-3.019944	-5.637718	7.834990
H	-3.172345	-8.797018	6.819091
H	-4.036876	-5.344452	7.629142
O	-3.464771	-2.869996	8.157597
H	0.545146	-6.778454	8.214268
H	-3.959151	-2.781465	5.808050

H	-4.489861	-7.817561	7.527624
H	-1.551083	-2.648047	8.863630

$^3\pi,\pi^*_{THY}$ min

H	-3.452306	-2.118992	4.436314
C	-3.598499	-3.093875	4.906871
N	-2.296041	-3.737836	5.054916
C	-2.209920	-5.103930	4.795705
O	-3.175402	-5.764149	4.442466
N	-0.969937	-5.674683	4.975056
C	0.232784	-5.004002	5.293474
O	1.286736	-5.641789	5.311457
C	0.085804	-3.624824	5.625285
C	1.238526	-2.806626	6.046647
C	-1.273303	-3.026352	5.649127
H	-4.230434	-3.718559	4.279838
H	-1.397578	-1.950842	5.673910
H	1.145050	-2.591410	7.122157
H	1.244875	-1.841912	5.523492
H	2.177797	-3.332945	5.877188
H	-0.889458	-6.647865	4.710755
H	-3.648999	-7.750671	5.864557
C	-3.578693	-7.907445	6.943853
N	-2.613623	-6.967417	7.518637
C	-1.273914	-7.372761	7.599388
O	-0.906503	-8.476468	7.252717
N	-0.416911	-6.421783	8.113201
C	-0.704798	-5.094477	8.435183
O	0.176818	-4.340072	8.813442
C	-2.107066	-4.745756	8.250487
C	-2.568870	-3.372383	8.482510
C	-2.975528	-5.695661	7.808225
H	-3.241040	-8.920751	7.151712
H	-4.021131	-5.445002	7.654840
O	-3.715805	-3.005174	8.281662
H	0.560648	-6.689099	8.127625
H	-4.060472	-2.960564	5.889492
H	-4.550390	-7.736664	7.408273
H	-1.802326	-2.677069	8.862112

Point Charges for the ForU Force Field obtained using the RESP procedure.

P	P	1.196691867
OP1	O2	-0.772342133
OP2	O2	-0.772342133
O5	OS	-0.365054133
C5’	CT	-0.160070133
H5’	H1	0.101460867
H5’’	H1	0.101460867
C4’	CT	0.340945867
O4’	OS	-0.444804133
C1’	CT	0.024640867
H1’	H2	0.198475867
N1	N*	-0.050829133
C6	CM	0.002479867
H6	H4	0.215447867
C5	CM	-0.406277133
C4	C	0.839587867
N3	NA	-0.765728133
C2	C	0.808213867
O2	O	-0.645664133
C3’	CT	0.170355867
H3’	H1	0.110814867
C2’	CT	-0.208790133
H2’	HC	0.088890867
H2’’	HC	0.088890867
O3’	OS	-0.514301133
H14	H1	0.024734867
C7	C	0.544444867
H3	H	0.383510867
O4	O	-0.615519133
O7	O	-0.563028133
H7	HC	0.044991867