Supporting Information

Why Replacing Different Oxygen of Thymine with Sulfur Causes Distinct Absorption and Intersystem Crossing?

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S1. Cartesian coordinates of optimized structures

Unless indicated otherwise, structures were optimized with ωB97XD/6-311++g(2d,p). xyz coordinates in Angstrom.

Table S1. Thymine

S_0				S_1 (water)				T_1 (water)				S_1 (gas phase)			
C	-2.945762	-0.694981	-0.666907	C	-2.909875	-0.629050	-0.750426	C	-2.929810	-0.641264	-0.730843	N	-3.748655	0.446771	-0.674065
C	-1.006839	0.796881	-0.273583	C	-0.969207	0.789501	-0.288958	C	-0.965593	0.790787	-0.313395	C	-2.954626	-0.633724	-0.906192
C	-1.931606	1.901466	-0.063854	C	-1.853272	1.844318	0.067623	C	-1.841119	1.852172	0.062197	N	-1.624990	-0.446249	-0.549780
C	-3.246071	1.644717	-0.165521	C	-3.262872	1.547385	0.254145	C	-3.278365	1.528281	0.308287	C	-1.157330	0.722153	0.047455
H	-3.997808	2.410187	-0.024612	H	-3.983226	2.239771	0.660440	H	-3.996928	2.319476	0.461917	C	-2.002628	1.796529	0.275023
O	-3.382946	-1.801219	-0.925694	O	-3.385348	-1.615949	-1.278475	O	-3.383139	-1.669015	-1.195215	C	-3.314085	1.647940	-0.097372
O	0.209225	0.881014	-0.214687	O	0.248383	0.881498	-0.508213	O	0.250567	0.891964	-0.464836	O	-3.338507	-1.677606	-1.383492
C	-1.375741	3.253704	0.251758	C	-1.400473	3.243296	0.147397	C	-1.385016	3.246598	0.170403	O	0.129344	0.683896	0.334560
H	-0.799358	3.230433	1.179386	H	-1.641309	3.662743	1.134181	H	-1.599202	3.634557	1.173841	C	-1.479482	3.057386	0.899859
H	-0.702865	3.591848	-0.539153	H	-0.331135	3.324808	-0.036402	H	-0.321582	3.340545	-0.038132	H	-4.057927	2.417670	0.030450
H	-2.176368	3.985393	0.361231	H	-1.941543	3.870633	-0.574804	H	-1.951548	3.880328	-0.523223	H	-1.065291	2.865510	1.892071
N	-1.601706	-0.426945	-0.559990	N	-1.583501	-0.490619	-0.420219	N	-1.582229	-0.458563	-0.503161	H	-0.690910	3.503982	0.290271
H	-0.980810	-1.209955	-0.712264	H	-0.982147	-1.215500	-0.786819	H	-0.984874	-1.206393	-0.824583	H	-2.281781	3.787771	1.003749
N	-3.739344	0.398552	-0.454102	N	-3.713370	0.446397	-0.387742	N	-3.727176	0.423825	-0.385105	H	-1.022455	-1.244798	-0.659250
H	-4.733787	0.249670	-0.520912	H	-4.702890	0.311532	-0.560634	H	-4.715773	0.277467	-0.527058	H	-4.712880	0.322323	-0.930417

Table S2. 2tThy

S_0				S_1 (water)				T_1 (water)				S_1 (gas phase)			
C	-3.198328	-0.464824	0.406909	N	-1.812458	-0.393339	0.564053	C	-3.172019	-0.453359	0.340478	N	-1.827334	-0.390786	0.506205
C	-1.058615	0.699983	0.021943	C	-3.193236	-0.497647	0.446440	C	-1.027942	0.754713	0.279536	C	-3.209771	-0.486650	0.465415
C	-1.799969	1.926992	-0.222913	N	-3.844849	0.727222	0.400820	C	-1.727901	1.937109	-0.091900	N	-3.852286	0.731145	0.335265
C	-3.139461	1.870645	-0.137601	C	-3.182787	1.890877	0.147251	C	-3.214783	1.936635	0.027844	C	-3.180295	1.902346	0.124580
H	-3.771371	2.732418	-0.304767	C	-1.838212	1.960323	0.056073	H	-3.809871	2.761712	-0.330264	C	-1.839075	1.978393	0.051240
O	0.152447	0.586176	-0.015610	C	-1.069971	0.745890	0.326133	O	0.191597	0.618802	0.304732	C	-1.068306	0.753746	0.285704
C	-1.043652	3.171745	-0.554851	S	-3.900754	-1.711592	-0.613819	C	-1.046474	3.120911	-0.636821	S	-3.908265	-1.857597	-0.422034
H	-0.346482	3.425400	0.246396	O	0.152551	0.704996	0.383914	H	0.031752	2.981506	-0.671857	O	0.142940	0.699782	0.331442
H	-0.456498	3.033796	-1.465216	C	-1.102378	3.229382	-0.235122	H	-1.419766	3.334422	-1.646441	C	-1.091244	3.247307	-0.203547
H	-1.725327	4.008882	-0.703198	H	-3.812160	2.766764	0.047198	H	-1.286100	4.005517	-0.034145	H	-3.808977	2.780679	0.032798
S	-4.033142	-1.868345	0.775417	H	-0.389778	3.462163	0.559503	S	-3.981025	-1.909353	0.402304	H	-0.368348	3.437640	0.592354
N	-3.810708	0.713089	0.167514	H	-0.533579	3.151194	-1.165183	N	-3.796579	0.697772	0.005705	H	-0.525465	3.186505	-1.136203
H	-4.817861	0.720266	0.219112	H	-1.799275	4.062677	-0.331434	H	-4.782860	0.612790	-0.196715	H	-1.775113	4.095274	-0.269104
N	-1.846142	-0.413961	0.323371	H	-4.844612	0.746269	0.519835	N	-1.844097	-0.336952	0.647538	H	-4.851395	0.752401	0.438763
H	-1.348244	-1.276837	0.496875	H	-1.281199	-1.231706	0.748732	H	-1.357285	-1.196800	0.853385	H	-1.289762	-1.216712	0.721513

Table S3. 4tThy

S_0				S_1 (water)				T_1 (water)				S_1 (gas phase)			
C	-3.221247	-0.479439	0.397321	N	-1.849545	-0.436139	0.362328	C	-3.172256	-0.452279	0.225083	N	-1.847166	-0.427632	0.359255
C	-1.073380	0.682283	0.050111	C	-3.213053	-0.450129	0.523403	C	-1.049126	0.741363	0.373522	C	-3.218345	-0.455406	0.524336
C	-1.790402	1.901766	-0.209565	N	-3.827070	0.740518	0.284492	C	-1.712577	1.938005	0.037912	N	-3.830042	0.745187	0.282203
C	-3.140215	1.856553	-0.150509	C	-3.150749	1.901485	-0.101755	C	-3.217144	1.951861	0.311270	C	-3.152783	1.901751	-0.099469
H	-3.752045	2.729745	-0.333679	C	-1.808952	1.903194	-0.257845	H	-3.755880	2.818110	-0.047640	C	-1.802834	1.898278	-0.255652
C	-1.065961	3.170711	-0.533049	C	-1.110224	0.694914	-0.019118	C	-1.100965	3.075171	-0.669797	C	-1.114083	0.697873	-0.020418
H	-0.386627	3.448892	0.275140	O	-3.814395	-1.461620	0.856259	H	-0.039458	2.936837	-0.858186	O	-3.811710	-1.458117	0.853980
H	-0.464721	3.056136	-1.437325	S	0.589846	0.528584	-0.157243	H	-1.626083	3.212593	-1.622569	S	0.598981	0.506763	-0.169266
H	-1.775177	3.983945	-0.687925	C	-1.058533	3.135119	-0.669847	H	-1.266285	3.994672	-0.099260	C	-1.058410	3.134550	-0.666886
N	-3.830194	0.718764	0.140470	H	-3.767423	2.772650	-0.261638	N	-3.737801	0.717962	-0.176436	H	-3.761359	2.778962	-0.259045
H	-4.838448	0.728793	0.173463	H	-0.316476	3.413561	0.083639	H	-4.685624	0.657023	-0.511314	H	-0.320235	3.419663	0.087305
N	-1.846007	-0.413492	0.333642	H	-0.530266	2.975915	-1.614157	N	-1.881469	-0.315742	0.739308	H	-0.530220	2.979981	-1.611564
H	-1.365007	-1.283411	0.520008	H	-1.739102	3.976314	-0.801042	H	-1.432446	-1.193367	0.954440	H	-1.743978	3.971747	-0.799226
S	0.588128	0.528671	0.030053	H	-4.827252	0.751073	0.393826	S	0.604433	0.584872	0.421190	H	-4.828954	0.743906	0.395347
O	-3.820621	-1.503284	0.655834	H	-1.391740	-1.316080	0.538097	O	-3.709242	-1.540450	0.146467	H	-1.393797	-1.308147	0.538497

Table S4. 2,4dtThy

S_0				S_1 (water)				T_1 (water)				S_1 (gas phase)			
N	-1.865161	-0.458258	0.133124	N	-1.849597	-0.439399	0.257464	C	-3.194040	-0.460165	0.403929	N	-1.846393	-0.431888	0.255274
C	-3.216156	-0.537940	0.260610	C	-3.197739	-0.498714	0.178537	C	-1.061962	0.717162	0.041825	C	-3.205767	-0.508753	0.180092
N	-3.863201	0.597728	-0.079304	N	-3.814670	0.659732	-0.097117	C	-1.745469	1.900612	-0.213739	N	-3.817513	0.665878	-0.094459
C	-3.225653	1.724129	-0.511239	C	-3.143553	1.873525	-0.293316	C	-3.172452	1.904123	-0.160017	C	-3.145387	1.871026	-0.293482
C	-1.882396	1.794635	-0.634206	C	-1.797095	1.931963	-0.217287	H	-3.781790	2.771011	-0.343288	C	-1.790352	1.926455	-0.216111
C	-1.124262	0.621277	-0.289399	C	-1.095406	0.734827	0.066154	C	-1.054807	3.179383	-0.544725	C	-1.100466	0.736948	0.068687
S	-3.993426	-1.916362	0.789320	S	-4.031552	-1.942734	0.416010	H	-0.381999	3.469369	0.263878	S	-4.025151	-1.932846	0.410134
S	0.531816	0.490971	-0.366762	S	0.607536	0.618256	0.175149	H	-0.447408	3.062739	-1.443650	S	0.616030	0.605180	0.207279
C	-1.201976	3.037232	-1.109842	C	-1.043647	3.210682	-0.420485	H	-1.776144	3.978045	-0.707288	C	-1.043376	3.209249	-0.424645
H	-3.876246	2.554792	-0.748277	H	-3.770420	2.725984	-0.502749	S	-4.060125	-1.852131	0.768042	H	-3.763667	2.729237	-0.507418
H	-0.483048	3.390577	-0.368124	H	-0.469950	3.468154	0.474247	N	-3.822371	0.712866	0.148530	H	-0.460498	3.470132	0.462844
H	-0.648744	2.844972	-2.031586	H	-0.338645	3.119587	-1.251494	H	-4.828800	0.691823	0.191930	H	-0.350952	3.128234	-1.266779
H	-1.930945	3.825231	-1.297057	H	-1.724296	4.032763	-0.639190	N	-1.855157	-0.435186	0.346550	H	-1.731005	4.029249	-0.630872
H	-4.869519	0.590033	-0.001772	H	-4.819327	0.632279	-0.157057	H	-1.372913	-1.299170	0.533695	H	-4.820966	0.625263	-0.152397
H	-1.349175	-1.292957	0.379137	H	-1.386158	-1.308939	0.468901	S	0.615289	0.535132	0.020887	H	-1.389057	-1.305398	0.459619

Table S5. S_0 structures of 2tThd and 2tThy/2tThd with few water molecules

2tThd

C	-1.321093	0.409293	1.102469
C	-3.187901	-0.262125	-0.386371
C	-2.243308	-0.328744	-1.482470
C	-0.965094	-0.026612	-1.213605
H	-0.216504	-0.052129	-1.993535
O	-4.381455	-0.495556	-0.454629
C	-2.730168	-0.714666	-2.841143
H	-3.191303	-1.704163	-2.816290
H	-3.489116	-0.011408	-3.190456
H	-1.910981	-0.728577	-3.559462
N	-2.620309	0.111240	0.825619
H	-3.252918	0.169159	1.612689
N	-0.480387	0.331702	0.032405
C	0.968512	0.621854	0.104978
O	1.196861	1.939040	0.530815
C	2.176864	1.969784	1.567594
C	2.880931	0.616487	1.490868
C	1.785323	-0.310058	0.995555
H	1.301771	0.537203	-0.929113
H	1.669584	2.099054	2.527417
H	2.161571	-1.163787	0.435687
H	1.199620	-0.661345	1.843209
O	3.083225	2.994448	1.337611
H	2.721266	3.820782	1.668054
O	3.396341	0.174642	2.723556
H	4.170058	0.701952	2.939638
H	3.680045	0.703062	0.745517
S	-0.906723	0.826637	2.670914

2tThd with 6 water
(PBE+D3/6-311G(d,p))

C	-2.281369	3.984776	0.042709
C	-0.537212	3.380948	1.716628
C	-1.295012	2.185173	2.029450
C	-2.466955	1.985869	1.366907
H	-3.088453	1.101193	1.548560
O	0.538074	3.714653	2.238341
C	-0.763037	1.231815	3.054014
H	0.232821	0.864299	2.760203
H	-0.641276	1.736113	4.025654
H	-1.433428	0.372004	3.182928
N	-1.117807	4.187330	0.722820
H	-0.552895	5.031313	0.474428
N	-2.984032	2.856932	0.410939
C	-4.300410	2.447561	-0.166321
O	-4.133797	2.013337	-1.517262
C	-5.017093	2.715024	-2.427129
C	-6.031446	3.491291	-1.530148
C	-5.407896	3.505233	-0.129869
H	-5.549212	1.961697	-3.025280
H	-5.012900	4.493495	0.129007
H	-6.169419	3.228113	0.610287
O	-4.254420	3.479292	-3.330338
H	-3.682232	4.064520	-2.763354
O	-7.283452	2.823269	-1.488386
H	-7.725062	3.058672	-2.351556
H	-6.139329	4.513142	-1.927307
S	-2.706393	5.120340	-1.156937
H	-4.567527	1.562820	0.426954
O	-6.093175	5.379393	-4.389849
H	-5.380794	4.721862	-4.216234
H	-5.972889	6.019162	-3.645842
O	-8.171403	3.693877	-3.904073
H	-8.020131	2.995578	-4.562420
H	-7.467584	4.375509	-4.112533

2tThy with 6 water
(PBE+D3/6-311g(d,p))

C	-3.415875	-1.070430	0.318934
C	-1.282495	-0.212147	-0.562106
C	-1.628363	1.109234	-0.082621
C	-2.840215	1.265336	0.561011
H	-3.175476	2.248353	0.944989
O	-0.194565	-0.515815	-1.184060
C	-0.667012	2.243225	-0.300065
H	-1.051826	3.175918	0.137238
H	0.313626	2.002991	0.153068
H	-0.480911	2.387973	-1.380939
S	-4.526369	-2.412584	0.575855
N	-3.697765	0.198913	0.748041
N	-2.214197	-1.230243	-0.324561
O	-2.065717	-3.826054	-0.993490
H	-2.157561	-4.061823	-1.945348
H	-2.944903	-3.961523	-0.543788
O	-6.099763	0.103479	1.932048
H	-6.863740	0.524280	1.474936
H	-6.131668	-0.878518	1.771295
O	2.106601	0.379700	0.147256
H	2.581685	0.977881	-0.474256
H	1.325987	0.002015	-0.351072
H	-1.981734	-2.211100	-0.668156
H	-4.628105	0.335627	1.243331
O	-3.464815	4.118813	1.348078
H	-2.558411	4.510802	1.576609
H	-3.747881	4.499477	0.485627
O	-1.047341	5.114123	1.868717
H	-0.361533	4.494180	2.203960
H	-0.642132	5.691210	1.183384
O	0.399068	1.214994	-3.311797
H	0.214684	0.548644	-2.589031
H	1.267047	1.630978	-3.103280

O	-4.281550	-0.612353	1.357229
H	-4.030153	-0.744622	0.404692
H	-5.251658	-0.651076	1.355311
O	-5.573139	6.967157	-2.125443
H	-4.817630	6.585691	-1.638017
H	-6.285935	6.996683	-1.464946
O	0.951436	6.052711	0.746742
H	1.130191	5.358039	1.423680
H	1.565478	5.833311	0.025221
O	-3.440809	-0.664881	-1.266869
H	-2.469914	-0.645908	-1.223699
H	-3.680131	0.250510	-1.543515

Table S6. S_0 structures of thymine derivatives with few water molecules around

2tThy with 3 water molecules

C	-3.233899	-0.534326	0.235072
C	-1.015523	0.452389	-0.067461
C	-1.643426	1.703353	-0.437833
C	-2.989032	1.736460	-0.442839
H	-3.547238	2.625618	-0.705460
O	0.193330	0.254602	-0.011679
C	-0.784951	2.874022	-0.790754
H	-0.147652	3.155033	0.050636
H	-0.126718	2.632061	-1.628015
H	-1.396042	3.733313	-1.065404
S	-4.196666	-1.859654	0.636944
N	-3.757124	0.653001	-0.116207
N	-1.880581	-0.586108	0.242954
O	-1.279954	-3.269219	1.068347
H	-0.971699	-3.882155	0.395145
H	-2.249410	-3.297789	1.022251
O	-6.522183	1.194228	-0.237948
H	-7.033407	0.575274	-0.767318
H	-6.949164	1.201931	0.623647
O	2.483932	1.833920	-0.401854
H	3.183374	1.209928	-0.196312
H	1.658884	1.332223	-0.281580
H	-1.450668	-1.481195	0.503623
H	-4.780386	0.747576	-0.135088

4tThy with 3 water molecules

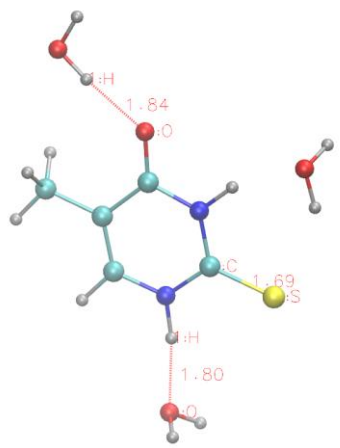
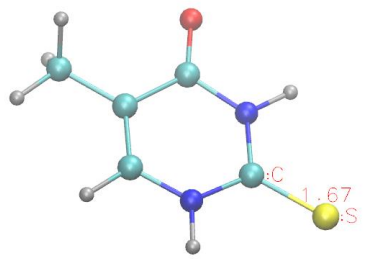
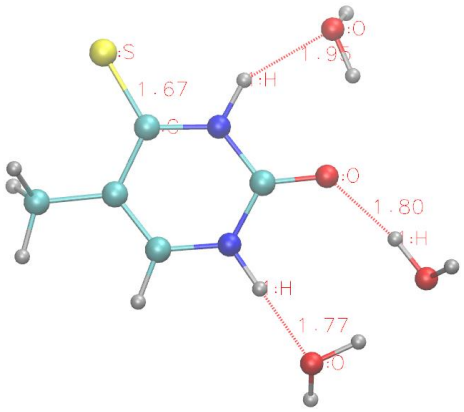
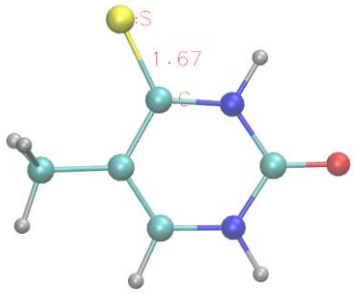
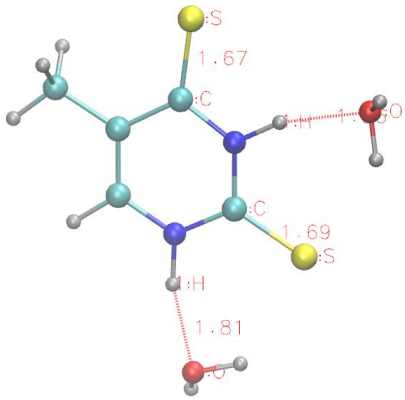
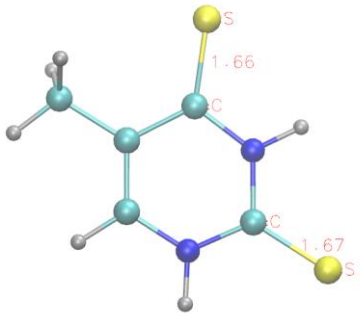
C	1.695662	-0.573925	-0.101265
C	-0.745114	-0.388043	-0.106085
C	-0.614814	1.042585	-0.086560
C	0.637889	1.553194	-0.075249
H	0.822003	2.619436	-0.059530
C	-1.820934	1.927980	-0.079561
H	-2.430420	1.760326	-0.970006
H	-2.450597	1.718797	0.787667
H	-1.526145	2.977175	-0.051674
N	1.758322	0.779791	-0.081663
H	2.689951	1.227605	-0.071265
N	0.428963	-1.092226	-0.112170
H	0.386403	-2.114700	-0.125000
S	-2.196184	-1.216399	-0.120970
O	2.687670	-1.305417	-0.108985
O	4.283442	1.988546	-0.124583
H	4.840878	1.183487	-0.165775
H	4.536487	2.445153	0.681771
O	1.343981	-3.813572	-0.203641
H	2.122128	-3.243188	-0.111030
H	1.330084	-4.365042	0.582704
O	5.340991	-0.523327	-0.243170
H	4.436026	-0.889434	-0.225364
H	5.720195	-0.801990	-1.080443

2,4dtThy with 2 water molecules

C	0.916629	0.538434	0.000263
C	-1.271180	-0.184288	0.797901
C	-1.873776	0.911065	0.089263
C	-1.048365	1.729174	-0.601959
H	-1.411664	2.579084	-1.164049
C	-3.351668	1.128750	0.115709
H	-3.875424	0.258133	-0.284510
H	-3.703164	1.274302	1.139235
H	-3.621253	2.003453	-0.475977
S	2.587944	0.313264	-0.051272
N	0.300138	1.546406	-0.643367
H	0.893760	2.191999	-1.180741
N	0.094981	-0.283690	0.695783
H	0.547072	-1.060850	1.194920
S	-2.105589	-1.305516	1.707543
O	2.296358	2.999274	-1.999127
H	2.925332	2.409917	-1.559094
H	2.513936	3.884473	-1.693224
O	1.816644	-2.206344	1.921240
H	1.796766	-3.106957	1.585583
H	2.498420	-1.750642	1.405898

S2. Solvent effects of water on the structures and absorption spectra

Table S7. The optimized structure of ground state of 2tThy, 4tThy, and 24dtThy

	With water molecules	No water molecule
2tThy		
4tThy		
2,4dtThy		

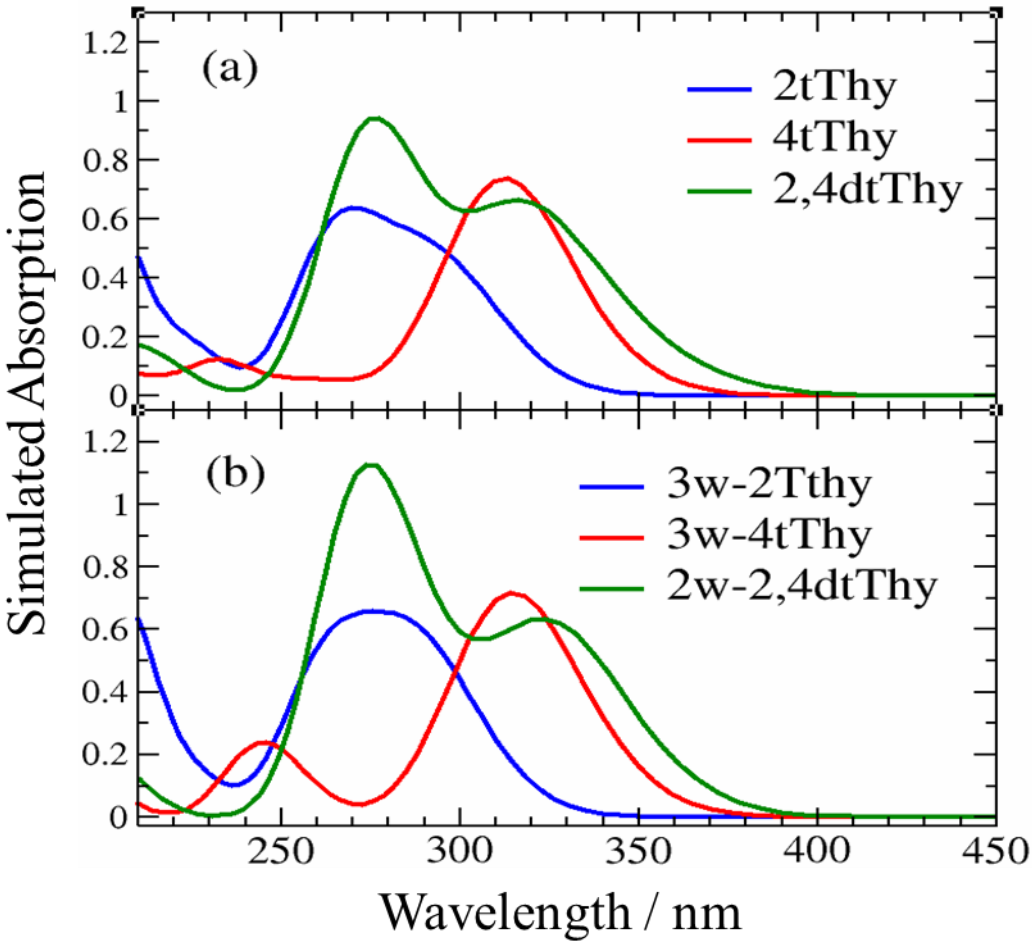


Figure S1. Absorption spectra with and without explicit water molecules.

(a) Calculated with continuum model; (b) calculated with explicit water molecules plus continuum model.

S3. MS-CASPT2 Vertical excitations from optimized S_0, S_1, and T_1 minima

Table S8. Thy

Geometry	State	Energy /eV	Osc. Str.	Character
Opt S_0	S_0	0.00	***	GS
	S_1	5.00	0.0003	nπ*
	S_2	5.03	0.3143	ππ*
	S_3	6.06	0.0496	ππ*
	S_4	6.36	0.0000	nπ*
	S_5	6.60	0.4292	ππ*
Opt S_1 water	S_0	0.00	**	GS
	S_1	3.82	**	ππ*
	S_2	4.20	**	nπ*
	T_1	2.56	**	ππ*
	T_2	4.17	**	nπ*
Opt S_1 gas phase	S_0	0.00	**	GS
	S_1	3.93	**	nπ*
	S_2	4.40	**	ππ*
	T_1	3.47	**	ππ*
	T_2	3.84	**	nπ*
Opt T_1 water	S_0	0.00	**	GS
	S_1	3.54	**	ππ*
	S_2	4.19	**	nπ*
	T_1	2.36	**	ππ*
	T_2	4.14	**	nπ*

Table S9. 2tThy

Geometry	State	Energy /eV	Osc. Str.	Character
Opt S_0	S_0	0.00	***	GS
	S_1	3.96	0.0000	nπ*
	S_2	4.34	0.5784	ππ*
	S_3	4.73	0.0843	ππ*
	S_4	4.78	0.0004	nπ*
Opt S_1 water	S_0	0.00	**	GS
	S_1	2.40	**	ππ*+nπ*
	S_2	3.01	**	nπ*+ππ*
	T_1	2.08	**	ππ*
	T_2	2.32	**	nπ*
Opt S_1 gas phase	S_0	0.00	**	GS
	S_1	2.52	**	nπ*+ππ*
	S_2	3.15	**	ππ*+nπ*
	T_1	2.30	**	ππ*
	T_2	2.40	**	nπ*
Opt T_1 water	S_0	0.00	**	GS
	S_1	3.02	**	ππ*

	S_2	3.40	**	nπ*
	T_1	2.23	**	ππ*
	T_2	3.44	**	nπ*

Table S10. 4tThy

Geometry	State	Energy /eV	Osc. Str.	Character
Opt S_0	S_0	0.00	**	GS
	S_1	3.04	0.0000	nπ*
	S_2	4.00	0.6623	ππ*
	S_3	4.80	0.0194	ππ*
	S_4	5.08	0.0000	nπ*
Opt S_1 water	S_0	0.00	**	GS
	S_1	2.72	**	nπ*
	S_2	4.00	**	ππ*
	T_1	2.68	**	ππ*
	T_2	2.70	**	nπ*
Opt S_1 gas phase	S_0	0.00	**	GS
	S_1	2.75	**	nπ*
	S_2	3.63	**	ππ*
	T_1	2.66	**	ππ*
	T_2	2.70	**	nπ*
Opt T_1 water	S_0	0.00	**	GS
	S_1	1.98	**	nπ*
	S_2	2.52	**	ππ*
	T_1	1.22	**	ππ*
	T_2	2.01	**	nπ*

Table S11. 2,4dtThy

Geometry	State	Energy /eV	Osc. Str.	Character
Opt S_0	S_0	0.00	**	GS
	S_1	2.97	0.0000	nπ*
	S_2	3.72	0.2157	ππ*
	S_3	3.92	0.0000	nπ*
	S_4	4.13	0.1564	ππ*
Opt S_1 water	S_0	0.00	**	GS
	S_1	2.64	**	nπ*
	S_2	3.53	**	ππ*
	T_1	2.60	**	ππ*
	T_2	2.62	**	nπ*
Opt S_1 Gas phase	S_0	0.00	**	GS
	S_1	2.58	**	nπ*
	S_2	3.58	**	ππ*
	T_1	2.53	**	ππ*
	T_2	2.57	**	nπ*
Opt T_1	S_0	0.0	**	GS

water	S_1	2.53	**	nπ*
	S_2	3.34	**	ππ*
	T_1	2.28	**	ππ*
	T_2	2.50	**	nπ*

S4. Oscillator strength analysis

The absorption spectra of 2tThy and 2tThd in water reported in ref. [1] are shown in Figure S2. The first band in each one was fitted by a double Gaussian function defined as

$$\varepsilon(\Delta E) = \varepsilon_{\max,1} \exp\left(-\frac{\Delta E^2}{\omega_1^2}\right) + \varepsilon_{\max,2} \exp\left(-\frac{\Delta E^2}{\omega_2^2}\right). \quad \text{(S1)}$$

The fitting parameters are given in Table S12.

The oscillator strengths for the Gaussian peaks contributing to the bands are also given in Table S3. They were computed from the fitting parameters as[2]

$$f = 6.17 \times 10^{-5} \frac{n}{f_C^2} \omega \varepsilon_{\max}, \quad \text{(S2)}$$

where n = 1.34 is the refractive index of water. In this equation, ω is given in eV and $\varepsilon_{\max}$ in $M^{-1}.cm^{-1}$. $f_C = 3n^2/(2n^2 + 1)$ is the local field correction as given by the free cavity model.

Using the same procedure, the experimental band maxima and oscillator strengths for all species have been extracted as well. They are reported in Table S13.

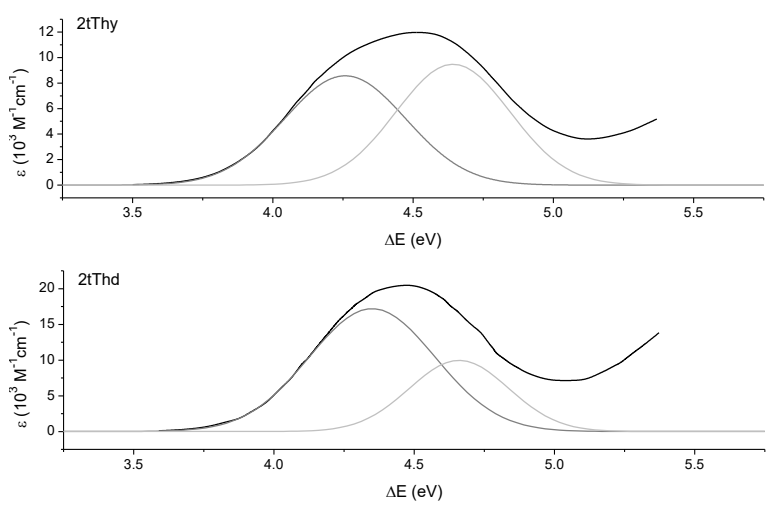


Figure S2. Gaussian fitting of experimental absorption spectra of 2tThy and 2tThd in water.

Table S12. Fitting parameters and oscillator strengths for 2tThy and 2tThd in water.

	2tThy		2tThd	
	Peak 1	Peak 2	Peak 1	Peak 2
ΔE (eV)	4.258	4.642	4.350	4.660
ε_{max} (10^3 $M^{-1}cm^{-1}$)	8.568	9.480	17.201	9.971
ω (eV)	0.306	0.287	0.317	0.250
f	0.158	0.163	0.327	0.150

Table S13. Experimental band maxima (eV) and oscillator strengths (in parentheses).

	Peak 1	Peak 2	Peak 3	Peak 4
Thy	4.641 (0.185)	-	-	-
2tThy	4.258 (0.158)	4.642 (0.163)	-	-
2tThd	4.350 (0.327)	4.660 (0.150)	-	-
4tThy	3.720 (0.222)	-	-	-
2,4dtThy	3.388 (0.096)	3.692 (0.123)	4.426 (0.355)	4.945 (0.182)

We have also fitted the experimental spectra for 2tThy and 2tThd in acetonitrile from ref. [3]. The fitting parameters and the oscillator strengths are given in Table S14.

Table S14. Fitting parameters and oscillator strengths for 2tThy and 2tThd in acetonitrile.

	2tThy		2tThd	
	Peak 1	Peak 2	Peak 1	Peak 2
ΔE (eV)	4.167	4.567	4.167	4.510
ε_{max} (10^3 $M^{-1}cm^{-1}$)	9.491	11.311	4.401	14.137
ω (eV)	0.232	0.308	0.185	0.420
f	0.132	0.209	0.049	0.357

The oscillator strength was obtained from the nuclear ensemble simulations by also fitting the spectrum with a double Gaussian function, Eq. S1. Because these spectra are given in terms of cross sections, rather

than in terms of molar attenuation coefficients, ε_{max} is replaced by σ_{max}. In this case, for cross sections given in Å^2.molecule^{-1}, the oscillator strength is

$$f = 1.61 \frac{n}{f_C^2} \omega \sigma_{max}. \quad \text{(S3)}$$

The fitting results and the oscillator strengths for 2tThy and 2tThd are given in 0 (gas phase) and Table S16 (water; continuum model only)

Table S15. Nuclear ensemble simulations of 2tThy and 2tThd in the gas phase.

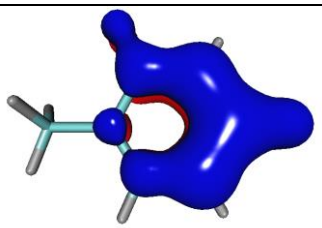
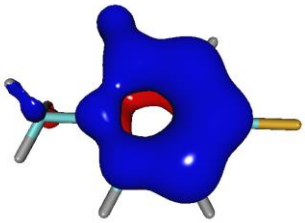
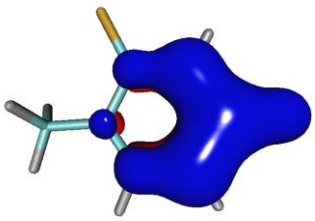
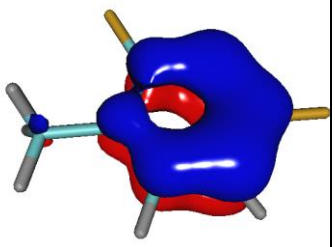
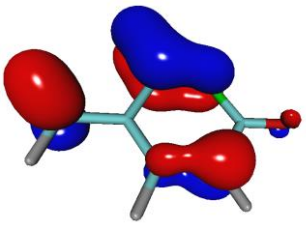
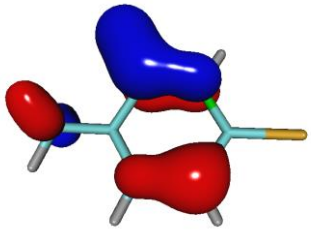
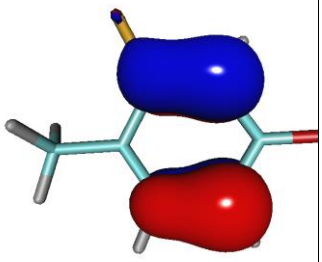
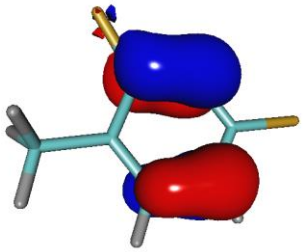
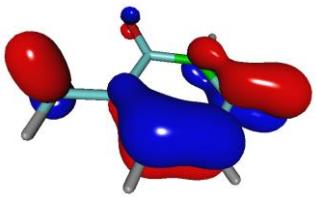
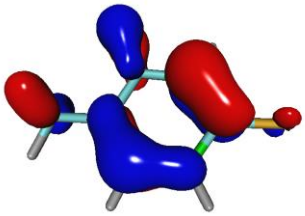
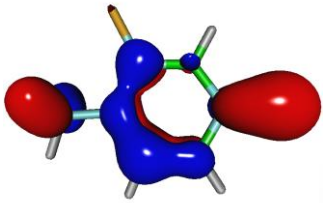
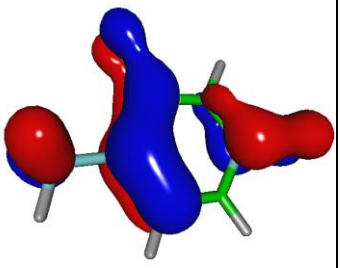
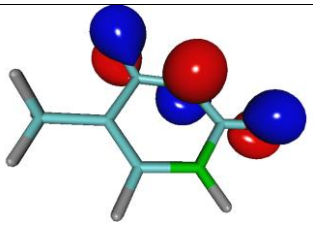
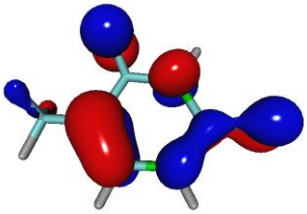
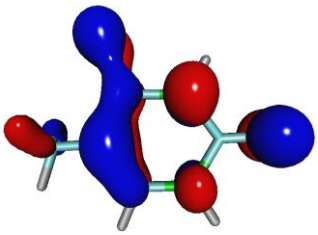
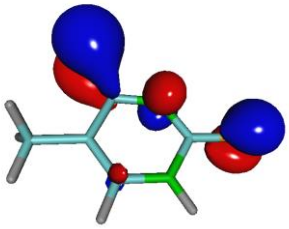
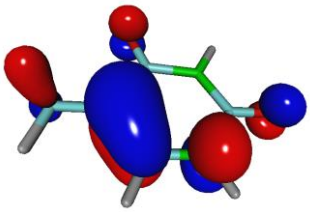
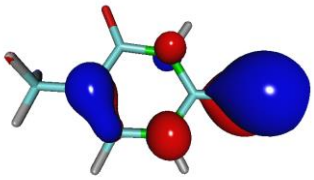
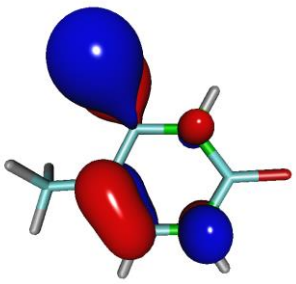
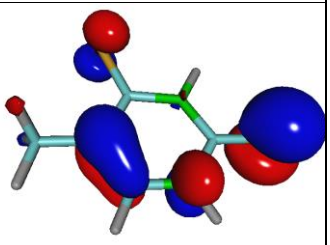
	2tThy		2tThd	
	Peak 1	Peak 2	Peak 1	Peak 2
ΔE (eV)	4.031	4.739	4.238	4.711
σ_{max} (Å^2.molecule^{-1})	0.120	0.698	0.189	0.462
ω (eV)	0.358	0.313	0.404	0.266
f	0.069	0.353	0.123	0.198

Table S16. Nuclear ensemble simulations of 2tThy and 2tThd in water.

	2tThy		2tThd	
	Peak 1	Peak 2	Peak 1	Peak 2
ΔE (eV)	4.284	4.697	4.348	4.694
σ_{max} (Å^2.molecule^{-1})	0.407	0.710	0.464	0.338
ω (eV)	0.369	0.232	0.382	0.214
f	0.235	0.258	0.278	0.113

S5. Relevant molecular orbitals for the absorption spectra

Table S17. Kohn-Sham π orbitals in the DFT/MRCI calculations.

	Thy	2tthy	4tthy	24dtthy
5				
4				
3				
2				
1				

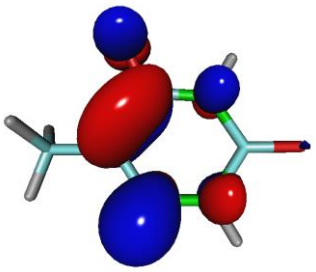
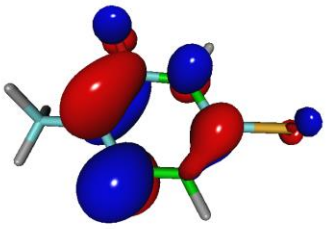
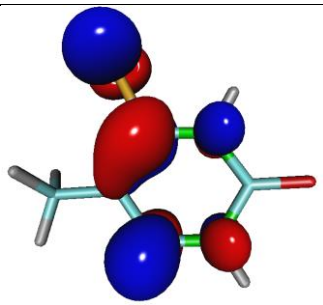
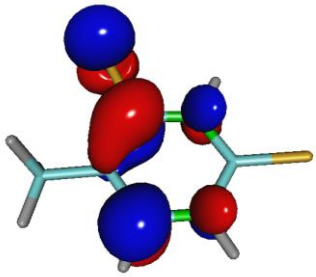
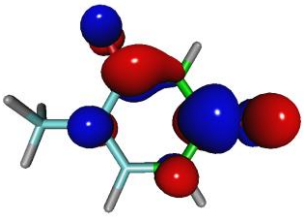
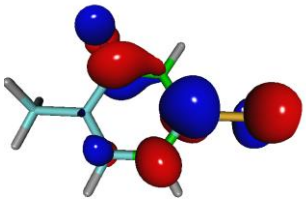
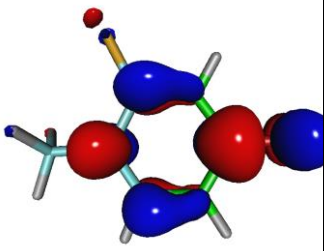
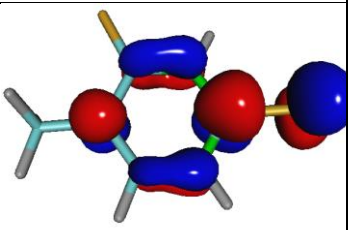
1’				
2’				

Table S18. CASSCF π orbitals in the CASPT2 calculations.

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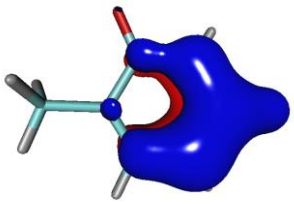
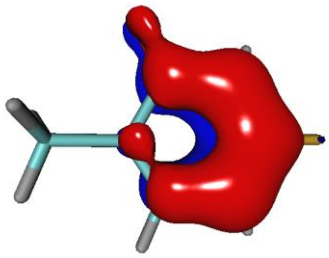
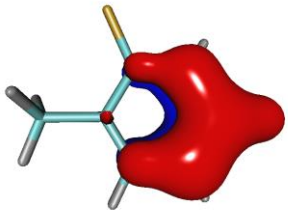
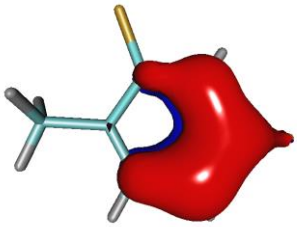
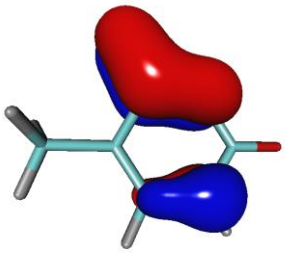
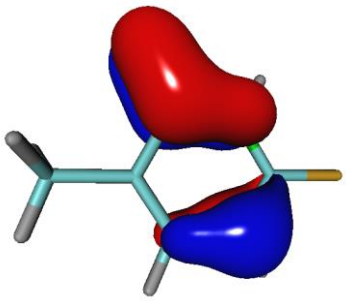
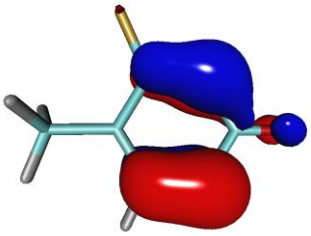
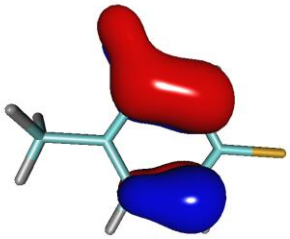
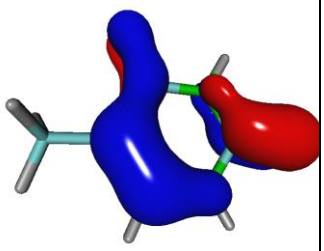
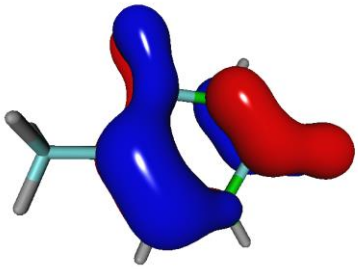
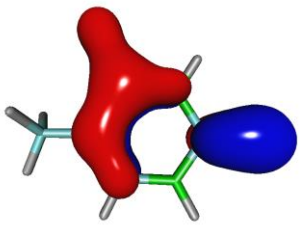
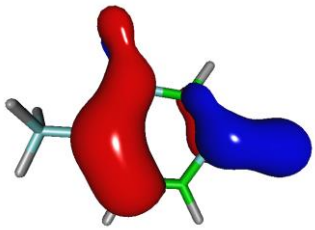
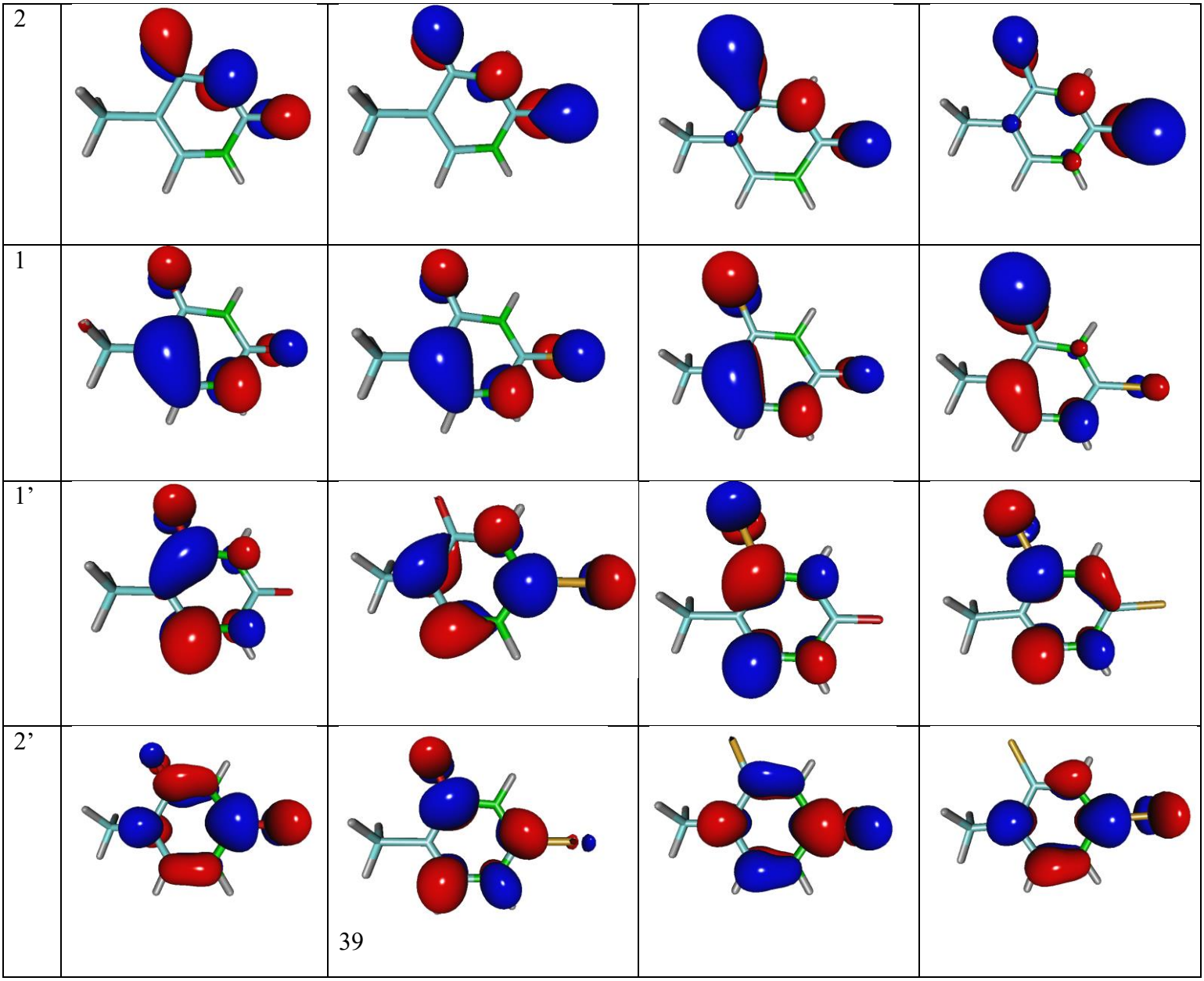
5				
4				
3				



The CASSCF frontier occupied molecular orbitals for S_1, T_1, and T_2 states at the S_1 minimum of 2tThy and 4tThy are shown in Figure S3 (a) and (b) respectively.

S6. Hückel model and red shift of thio-substituted thymines

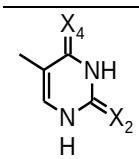
The replacement of one or both oxygen atoms in thymine by sulfur leads to a strong red shift in the lowest electronic transitions (Table S19). We can understand the origin of this shift by considering the Hückel model for a C=X bond (X = O or S). The Hamiltonian in this case is simply[4]

$$H = \begin{bmatrix} \alpha & \beta_X \\ \beta_X & \alpha_X \end{bmatrix}, \tag{S4}$$

where

$$\begin{aligned} \alpha_X &= \alpha + h_X \beta, \\ \beta_X &= K_X \beta. \end{aligned} \tag{S5}$$

Table S19. Lowest electronic transition in thio-substituted thymine computed with DFT/MRCI.

	X_2	X_4	ΔE (eV)	Character (% π_H-π_L)
Thy	O	O	5.26	88
2tThy	S	O	4.20	88
4tThy	O	S	3.97	84
2,4dtThy	S	S	3.61	81

The eigenvalues of H are

$$\varepsilon_{\pm} = \alpha + \frac{1}{2}\left(h_X \pm \sqrt{h_X^2 + 4K_X^2}\right)\beta, \tag{S6}$$

leading to an electronic energy gap

$$\Delta\varepsilon_X = \varepsilon_+ - \varepsilon_- = -\beta\sqrt{h_X^2 + 4K_X^2}. \tag{S7}$$

Considering the Hückel parameters in Table S20, the ratio between the electronic gap for C=O ad C=S is

$$\frac{\Delta\varepsilon_O}{\Delta\varepsilon_S} = \sqrt{\frac{h_O^2 + 4K_O^2}{h_S^2 + 4K_S^2}} \approx 1.4. \tag{S8}$$

Thus, Hückel theory predicts a red-shift factor of 1.4 for a thio-substitution of a C=O group, basically the same shift factor predicted by DFT/MRCI for the ratio between transition energies of Thy and 2,4dtThy, which is 1.5. This factor is also in perfect agreement with the experimental data from ref. [1], which is also 1.4.

According to Eq. (S8), the source of the red-shift factor can be traced back mainly to the fact that $K_O > K_S$, meaning that the shift is a consequence of the weaker C=S bond as compared to the C=O bond.

Table S20. Hückel parameters.

$X =$	C	N	O	S
h_X	0.00	1.37	0.97	0.46
K_X	1.00	0.89	1.06	0.81

S7. NBO analysis

Table S21. NBO distribution along C=O and C=S π bonds.

Analysis based on Kohn-Sham orbitals computed at BHLYP/def2-TZVP level.

	π(C_2=O/S_2)			π(C_4=O/S_4)		
	C_2	O_2	S_2	C_4	O_4	S_4
Thy	0.27	0.74	**	0.29	0.71	**
2tThy	0.61	**	0.39	0.29	0.71	**
4tThy	0.27	0.73	**	0.32	**	0.68
24dtThy	0.61	**	0.39	0.33	**	0.67

S8. SOC matrix elements and frontier occupied molecular orbitals

Table S22. Hyperfine SOC components for Thy, 2tThy, 4tThy and 24dtThy at the S_1 minima.

		S_1/T_1 (cm^{-1})			S_1/T_2 (cm^{-1})		
	Phase	$H^{so}_{s_1/t_{1,-1}}$	$H^{so}_{s_1/t_{1,0}}$	$H^{so}_{s_1/t_{1,1}}$	$H^{so}_{s_1/t_{2,1}}$	$H^{so}_{s_1/t_{2,0}}$	$H^{so}_{s_1/t_{2,1}}$
Thy	W	1	0	1	15	2	15
	GP	34	10	34	0	0	0
2tThy	W	55	69	55	57	73	57
	GP	84	84	84	45	48	45
4tThy	W	111	13	111	4	1	4
	GP	110	13	110	17	3	17
24dtThy	W	107	9	107	1	0	1
	GP	108	12	108	1	1	1

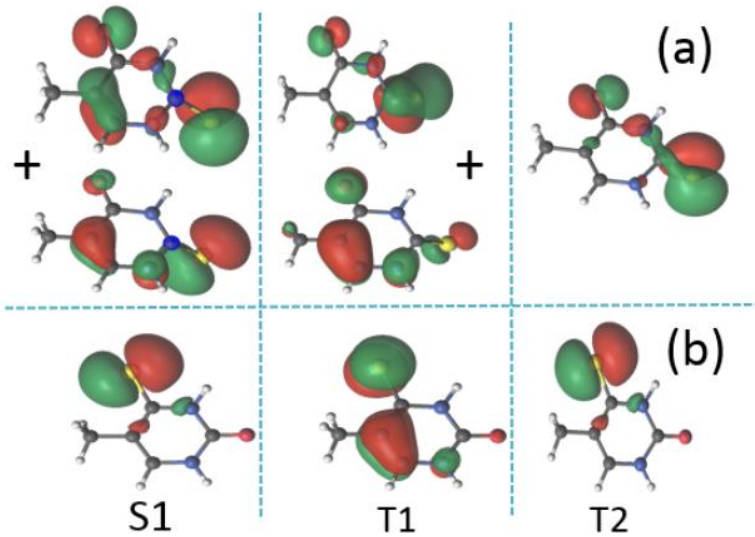


Figure S3. CASSCF frontier occupied molecular orbitals for SOC of 2tThy and 4tThy.

S9. Additional references

1. Pollum, M.; Jockusch, S.; Crespo-Hernández, C. E., 2,4-Dithiothymine as a Potent Uva Chemotherapeutic Agent. *J. Am. Chem. Soc.* **2014,** *136*, 17930-17933.
2. Parson, W. W., *Modern Optical Spectroscopy*. Springer-Verlag: Berlin Heidelberg, 2007.
3. Taras-Goślińska, K.; Burdziński, G.; Wenska, G., Relaxation of the T_1 Excited State of 2-Thiothymine, Its Riboside and Deoxyriboside-Enhanced Nonradiative Decay Rate Induced by Sugar Substituent. *J. Photochem. Photobiol. A* **2014,** *275*, 89-95.
4. Carissan, Y.; Hagebaum-Reignier, D.; Goudard, N.; Humbel, S., Hückel-Lewis Projection Method: A "Weights Watcher" for Mesomeric Structures. *J. Phys. Chem. A* **2008,** *112*, 13256-13262.