Supplementary Information *for*

Excited-state relaxation mechanism of potential UVA-activated phototherapy molecules: trajectory surface hopping simulations of both 4-thiothymine and 2,4-dithiothymine

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Table S1. Relative energies (eV) of the optimized structures of 4-thiothymine at different level of theory.

Minima structure	State	TD-B3LYP/6-31G*	MS-CASPT2//CAS(12,9)/ ANO-L[a]	Exp.[a]
4tT_S_0	S_0	0.00	0.0	
	$S_1(n_8\pi_8^*)$	2.90	2.87	
	$S_2(\pi_{56}\pi_8^*)$	4.61	4.17	3.70
	$S_3(\pi_8\pi_8^*)$	4.90		(335 nm)
4tT_$^1n_8\pi_8^*$	$S_1(n_8\pi_8^*)$	2.62	2.51	
4tT_$^1\pi_{56}\pi_8^*$	$S_2(\pi_{56}\pi_8^*)$	4.17	3.44	3.10
4tT_$^3\pi_{56}\pi_8^*$	$T_1(\pi_{56}\pi_8^*)$	2.17	2.34	2.29
4tT_$^3n_8\pi_8^*$	$T_2(n_8\pi_8^*)$	2.29		

[a] Ref. 10 in the main text.

Table S2. Relative energies (eV) of the optimized structures of 2,4-dithiothymine at different level of theory.

Minima	State	TD-B3LYP/6-31G*	MS-CASPT2//CAS(16,12)/ 6-31G*[a]	Exp.[b]
24dtT_S_0	S_0	0.00	0.00	
	$S_1(n_8\pi_8^*)$	2.87	2.90	
	$S_2(n_7\pi_7^*)$	3.55	3.69	
	$S_3(\pi_7\pi_8^*)$	3.59	3.71	3.39
				(365 nm)
24dtT_$^1n_8\pi_8^*$	$S_1(n_8\pi_8^*)$	2.60	2.56	
24dtT_$^1\pi_7\pi_8^*$	$S_2(\pi_7\pi_8^*)$	2.91	3.35	
24dtT_$^3\pi_8\pi_8^*$	$T_1(\pi_8\pi_8^*)$	2.14	2.33	2.29
24dtT_$^3n_8\pi_8^*$	$T_2(n_8\pi_8^*)$	2.26		

[a] ref.15 in the main text.
[b] ref.s 3 and 6 in the main text.

Table S3. Absolute values of the calculated singlet-triplet splitting at the optimized excited singlet state minima in vacuum at different level of theory.

4-thiothymine				
Minimum		MS-CASPT2 //CASSCF(12,9)/ANO-L [a]	TD-B3LYP/6-31G*	MS(6)-CASPT2(12,9)// TD-B3LYP/6-31G*
4tT_$^1n_8\pi_8^*$	S_1 -T_1:	0.04	0.26	0.05
	S_1 -T_2:	0.14	0.30	0.21
4tT_$^1\pi_{56}\pi_8^*$	S_2-T_3:		0.31	0.66
	S_2-T_2:	0.73	1.57	0.57

2,4-dithiothymine				
Minimum	TD// CAS(16,12)/6-31G*[b]	MS-CASPT2// CAS(16,12)/6-31G*[c]	TD-B3LYP// B3LYP/6-31G*	MS(6)-CASPT2(16,12)// B3LYP/6-31G*
24dtT_$^1n_8\pi_8$*	S_1- T_1: 0.27	0.02	0.27	0.01
	S_1- T_2: 0.29	0.01	0.30	0.16
24dtT_$^1\pi_7\pi_8$*	S_2-T_3: 0.13	0.11	0.09	0.08
	S_2-T_2: 0.27	0.48	0.17	0.25

[a] ref. 10 in the main text.

[b] the structures are taken from ref. 15 in the main text.

[c] ref. 15 in the main text.

Table S4. Absolute values of the calculated S_2-T_3 splitting (eV) at the twenty S_2/T_3 crossing points of 4-thiothymine in water at different level of theory.

Points	TD-B3LYP/6-31G*	MS(6)-CASPT2(12,9)//TD-B3LYP6-31G*
Point 1	0.12	0.28
Point 2	0.15	0.13
Point 3	0.15	0.11
Point 4	0.1	0.07
Point 5	0.01	0.18
Point 6	0.25	0.01
Point 7	0.42	0.08
Point 8	0.29	0.14
Point 9	0.12	0.14
Point 10	0.18	0.13
Point 11	0.47	0.57
Point 12	0.13	0.19
Point 13	0.11	0.08
Point 14	0.04	0.08
Point 15	0.2	0.26
Point 16	0.1	0.05
Point 17	0.21	0.04
Point 18	0.16	0.32
Point 19	0.2	0.16
Point 20	0.16	0.13

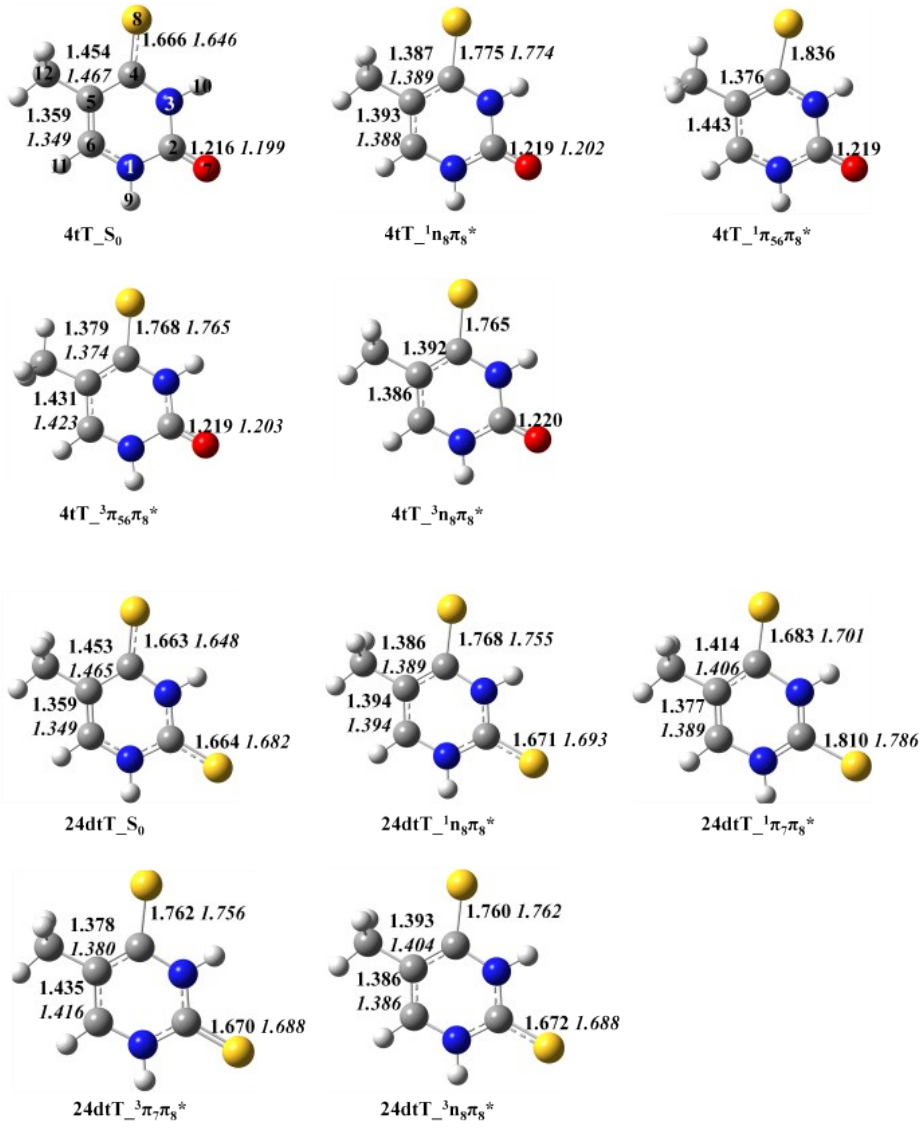

Figure S1. Some key geometrical parameters (bond-length unit in angstrom, Å) of the optimized structures in different electronic states, along with the atom numbering scheme in the S_0 minimum of 4-thiothymine (4tT_S_0). The excited state minima of 4-thiothymine in the S_1, S_2, T_1, and T_2 surfaces, of $n_8\pi_8^*$, $\pi_{56}\pi_8^*$, $\pi_{56}\pi_8^*$, and $n_8\pi_8^*$ character, are referred as 4tT_$^1n_8\pi_8^*$, 4tT_$^1\pi_{56}\pi_8^*$, 4tT_$^3\pi_{56}\pi_8^*$, and 4tT_$^3n_8\pi_8^*$, respectively, in this figure. For 2,4-dithiothymine, the minimum in the S_0 state and the excited S_1, S_2, T_1, and T_2 surfaces, of $n_8\pi_8^*$, $\pi_7\pi_8^*$, $\pi_8\pi_8^*$, and $n_8\pi_8^*$ character, are referred as 24dtT_S_0, 24dtT_$^1n_8\pi_8^*$, 24dtT_$^1\pi_7\pi_8^*$, 24dtT_$^3\pi_7\pi_8^*$, and 24dtT_$^3n_8\pi_8^*$, respectively, in this figure. See Section S1 of ESI for Cartesian coordinates of these structures. The italic ones for 4-thiothymine are from optimizations at the CAS(12,9)/6-31G* level, and the italic ones for 2,4-dithiothymine are taken from ref.

15 in the main text.

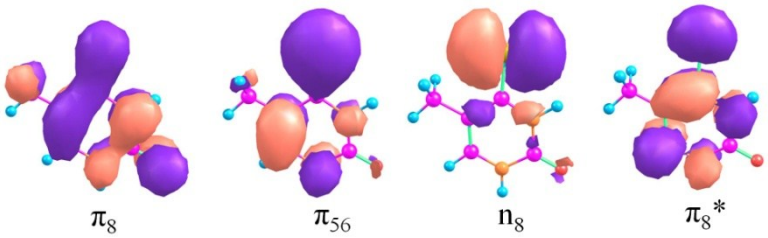

Figure S2. The molecular orbitals at the Franck-Condon geometry of 4-thiothymine optimized at the B3LYP/6-31G* level.

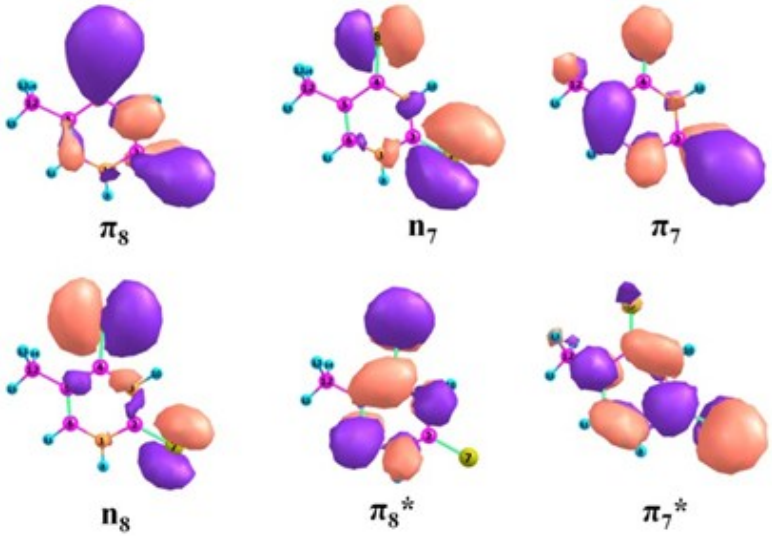

Figure S3. The molecular orbitals at the Franck-Condon geometry of 2,4-dithiothymine optimized at the B3LYP/6-31G* level.

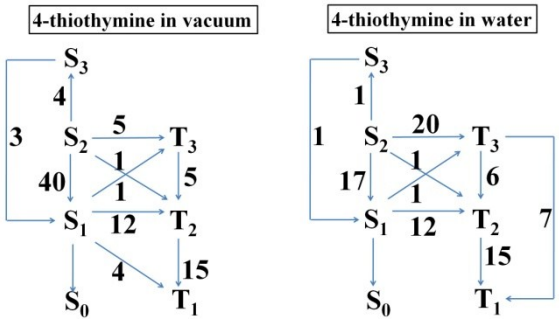

Figure S4. Net population transfer (numbers of trajectories) among the electronic states of 4-thiothymine.

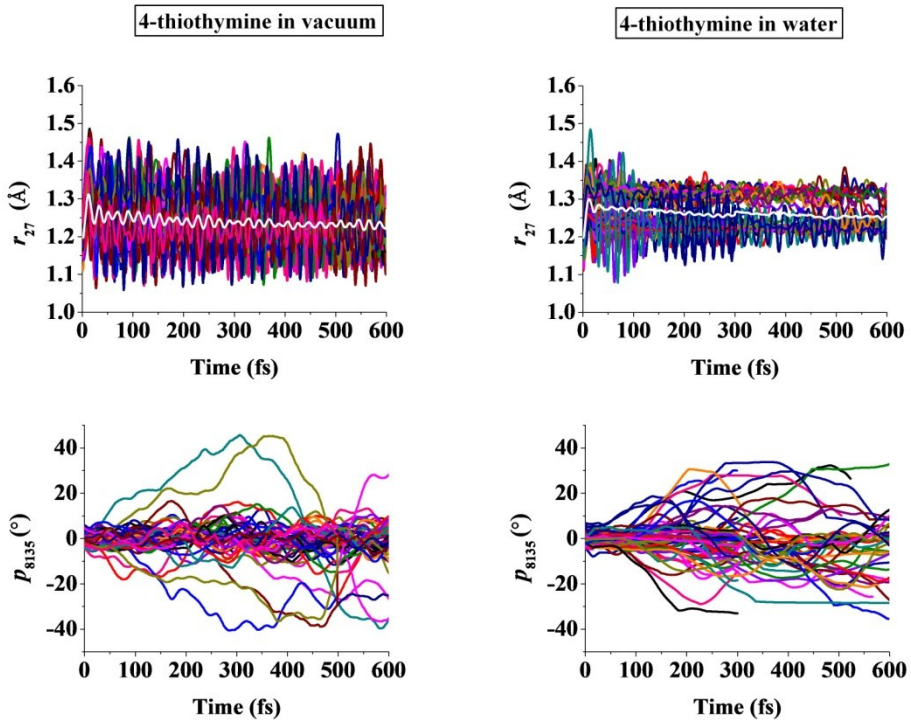

Figure S5. Time-evolution of the C2-O7 (r_{27}) bond-length and its ensemble-averaged value (the white line), as well as the S8−N1−N3−C5 pyramidalization angle (p_{8135}) for 4-thiothymine. Bond-length unit in angstrom, Å, and pyramidalization angle unit in degrees, °. Different trajectories are coded by color.

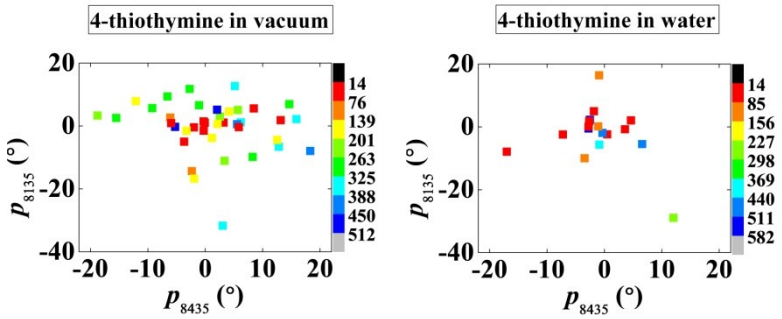

Figure S6. Distribution of p_{8435} vs. p_{8135} of the $S_2 \rightarrow S_1$ crossing points for 4-thiothymine. Bond-length unit in angstrom, Å, and pyramidalization angle unit in degrees, °.

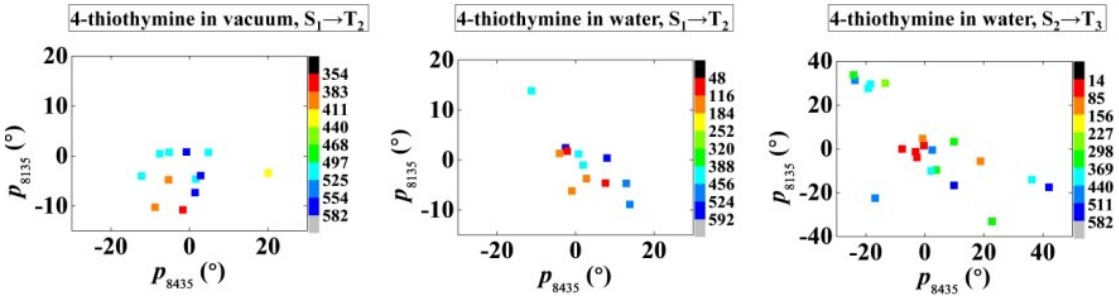

Figure S7. Distribution of p_{8435} vs. p_{8135} of the singlet → triplet crossing points for 4-thiothymine. Bond-length unit in angstrom, Å, and pyramidalization angle unit in

degrees, °.

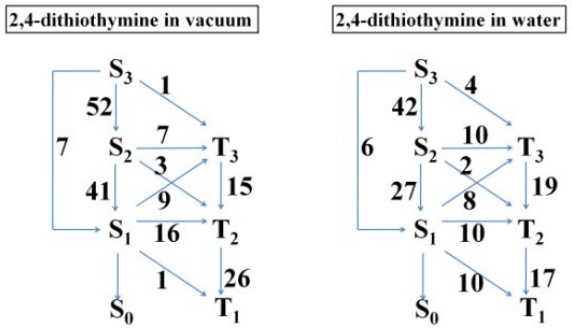

Figure S8. Net population transfer (numbers of trajectories) among the electronic states of 2,4-dithiothymine.

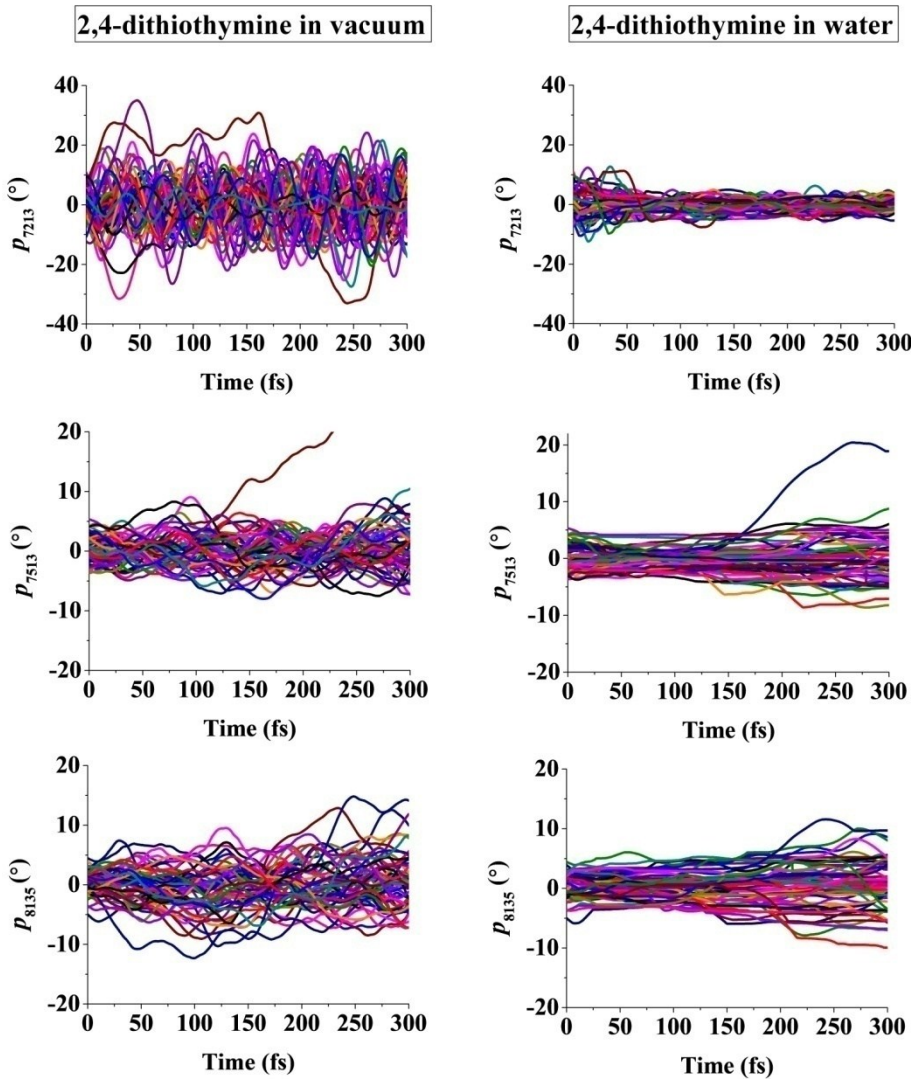

Figure S9. Time-evolution of the S7−C2−N1−N3 (p_{7213}), S7−C5−N1−N3 (p_{7513}), and S8−N1−N3−C5 (p_{8135}) pyramidalization angles of 2,4-dithiothymine. Pyramidalization angle unit in degrees, °. Different trajectories are coded by color.

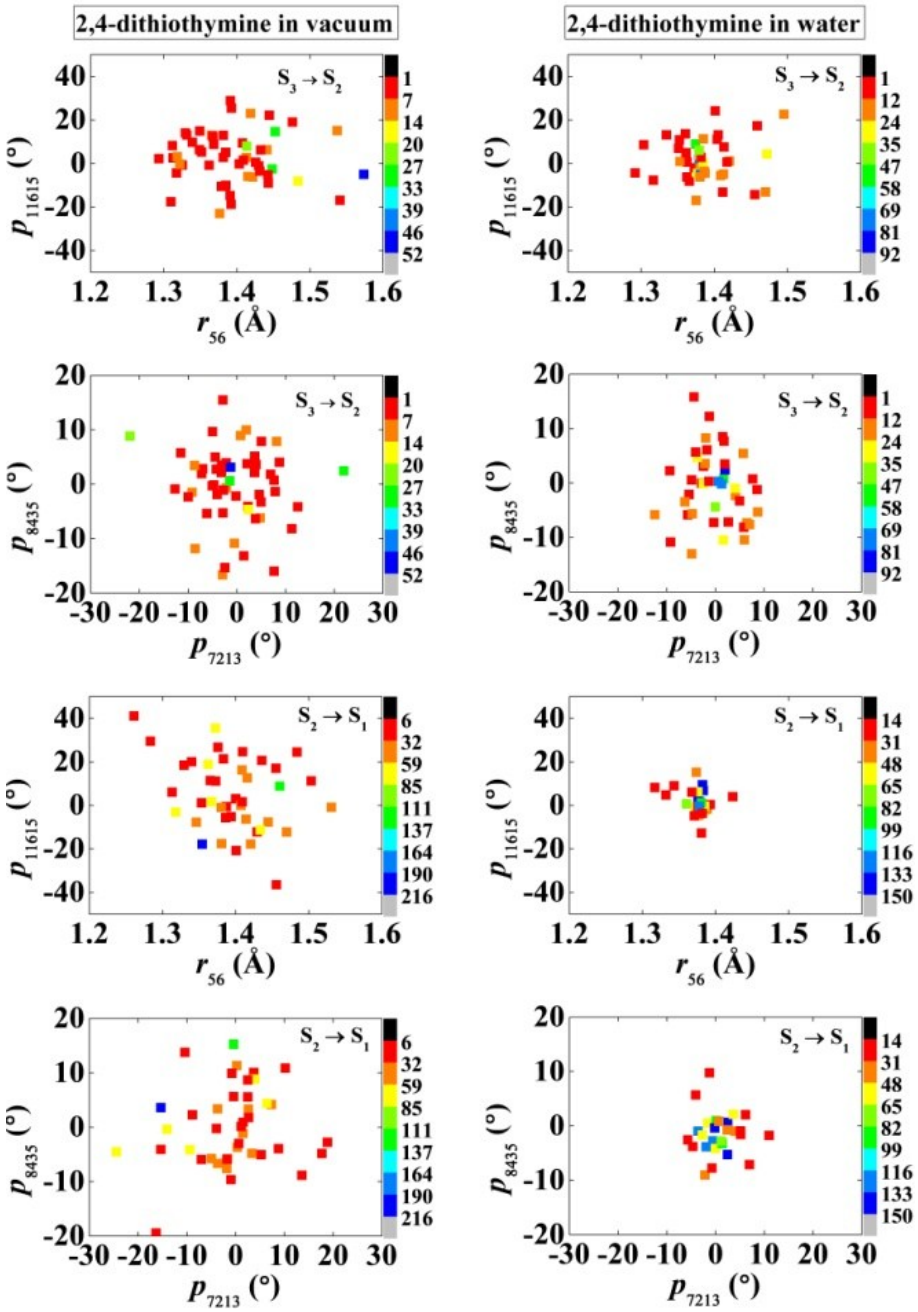

Figure S10. Distribution of both hopping time and key geometrical parameters at the $S_3 \rightarrow S_2$ and $S_2 \rightarrow S_1$ hopping points for 2,4-dithiothymine. Bond-length unit in angstrom, Å, and pyramidalization angle unit in degrees, °.

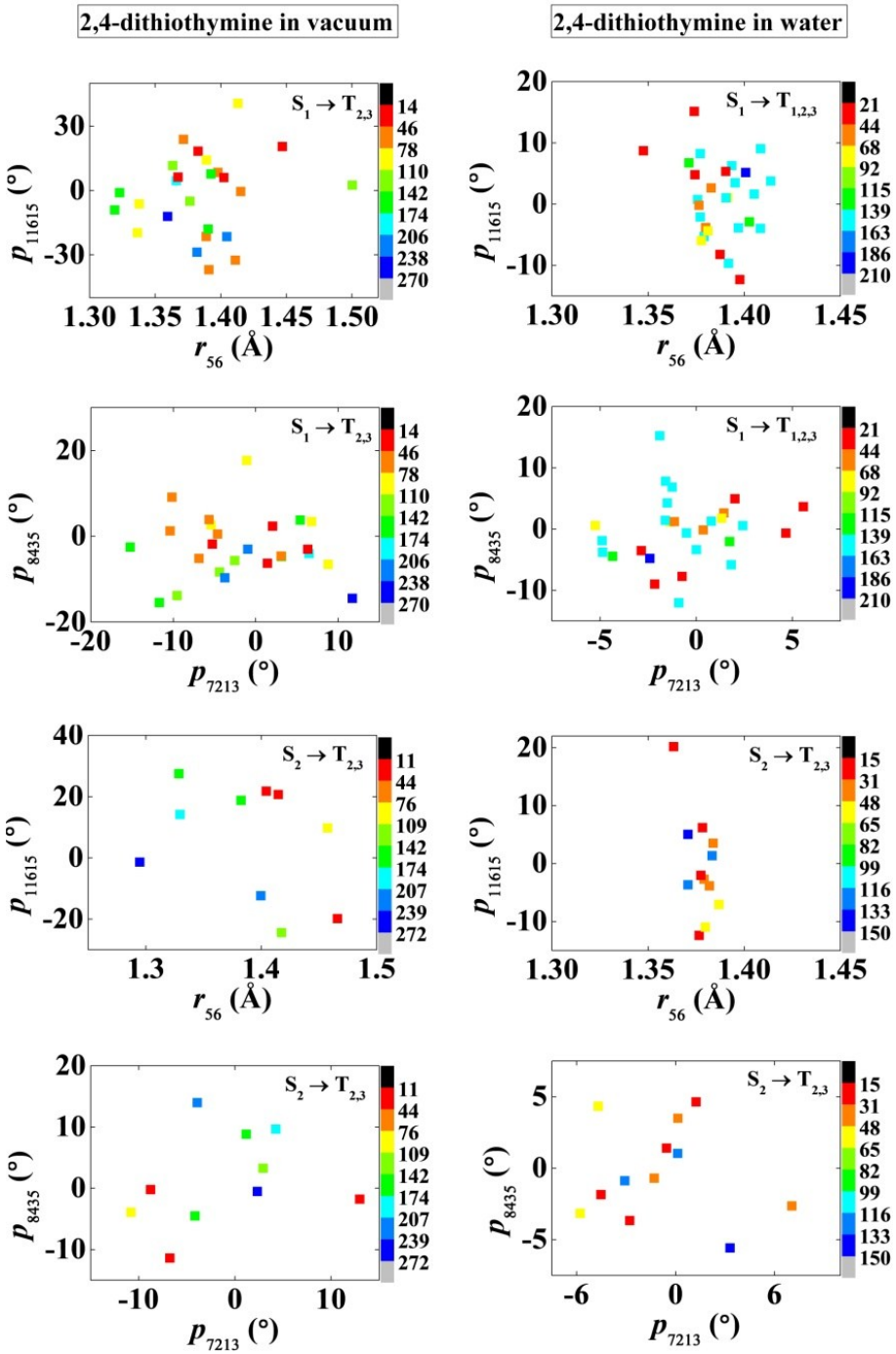

Figure S11. Distribution of bond-length and pyramidalization angles at the singlet-to-triplet crossing points (including $S_1 \rightarrow T_{2,3}$ and $S_2 \rightarrow T_{2,3}$ in vacuum, and $S_1 \rightarrow T_{1,2,3}$ and $S_2 \rightarrow T_{2,3}$ in water) for 2,4-dithiothymine. Bond-length unit in angstrom, Å, and pyramidalization angle unit in degrees, °.

S1. Cartesian coordinates of the structures optimized at the (TD-)B3LYP/6-31G* level.

4tT_S_0

N	0.131680000	0.002151000	-3.145002000
C	0.066855000	-1.315037000	-2.707856000

N	0.001749000	-1.408106000	-1.323661000
C	-0.004026000	-0.382606000	-0.386965000
C	0.067704000	0.957715000	-0.945022000
C	0.132220000	1.084160000	-2.296673000
O	0.065398000	-2.273746000	-3.456318000
S	-0.089025000	-0.740703000	1.237537000
H	0.180656000	0.121518000	-4.147753000
H	-0.047745000	-2.354745000	-0.961409000
H	0.187454000	2.052109000	-2.783624000
C	0.069242000	2.157498000	-0.040320000
H	-0.834361000	2.182028000	0.577983000
H	0.918844000	2.125920000	0.650168000
H	0.123208000	3.083690000	-0.621642000

4tT_$^{1}n_{8}\pi_{8}$*

N	0.132026000	-0.009513000	-3.152440000
C	0.065673000	-1.312550000	-2.708394000
N	-0.000025000	-1.415567000	-1.319624000
C	-0.000891000	-0.335394000	-0.434834000
C	0.066841000	0.954274000	-0.940473000
C	0.134158000	1.112888000	-2.323056000
O	0.065756000	-2.286829000	-3.441065000
S	-0.090945000	-0.762699000	1.286104000
H	0.180278000	0.088631000	-4.156786000
H	-0.047012000	-2.366507000	-0.980403000
H	0.189570000	2.073564000	-2.814397000
C	0.068340000	2.150981000	-0.022746000
H	-0.841141000	2.187992000	0.589772000
H	0.925211000	2.130647000	0.662174000
H	0.122015000	3.081928000	-0.594390000

4tT_$^{1}\pi_{56}\pi_{8}$*

N	0.120711000	0.004719000	-3.139603000
C	0.066894000	-1.309379000	-2.716765000
N	0.011794000	-1.392653000	-1.305460000
C	0.010606000	-0.337909000	-0.440256000
C	0.065871000	0.953955000	-0.910262000
C	0.122873000	1.112194000	-2.343651000
O	0.065884000	-2.283750000	-3.450067000
S	-0.071634000	-0.955145000	1.287258000
H	0.160877000	0.102387000	-4.148949000
H	-0.028864000	-2.326734000	-0.907656000
H	0.171120000	2.071295000	-2.840678000
C	0.068911000	2.172392000	-0.031776000
H	0.051291000	1.883901000	1.021550000
H	0.963384000	2.787636000	-0.202208000

H	-0.805063000	2.810502000	-0.224085000

4tT_$^3\pi_{56}\pi_8$*

N	-0.007897000	0.003449000	-3.138849000
C	0.060561000	-1.317911000	-2.702264000
N	0.129645000	-1.427076000	-1.328102000
C	0.134214000	-0.356947000	-0.410002000
C	0.063924000	0.931451000	-0.896183000
C	-0.010393000	1.115394000	-2.313524000
O	0.058805000	-2.265712000	-3.468193000
S	0.234705000	-0.828875000	1.290460000
H	-0.059536000	0.102922000	-4.144024000
H	0.182756000	-2.369731000	-0.966632000
H	-0.068447000	2.083442000	-2.789197000
C	0.062973000	2.160690000	-0.031053000
H	-0.832704000	2.765299000	-0.222737000
H	0.089758000	1.902983000	1.027936000
H	0.931492000	2.792472000	-0.258194000

4tT_$^3n_8\pi_8$*

N	0.131918000	-0.009530000	-3.151139000
C	0.067523000	-1.313770000	-2.707811000
N	0.001386000	-1.422651000	-1.322631000
C	0.000053000	-0.340545000	-0.430583000
C	0.066421000	0.953531000	-0.939521000
C	0.132295000	1.112140000	-2.315332000
O	0.067334000	-2.285470000	-3.445001000
S	-0.087096000	-0.753112000	1.283355000
H	0.179462000	0.091525000	-4.154685000
H	-0.044949000	-2.375469000	-0.990263000
H	0.185386000	2.074270000	-2.804420000
C	0.067315000	2.152347000	-0.023806000
H	-0.842894000	2.192449000	0.587447000
H	0.923888000	2.134497000	0.661577000
H	0.121814000	3.081635000	-0.597743000

24dtT_S_0

N	0.132107000	-0.004336000	-3.136272000
C	0.066332000	-1.305408000	-2.699953000
N	0.001507000	-1.404292000	-1.331887000
C	-0.004356000	-0.379511000	-0.388498000
C	0.067819000	0.961417000	-0.944304000
C	0.132980000	1.083985000	-2.296527000
S	0.064619000	-2.612360000	-3.730589000
S	-0.089448000	-0.747067000	1.230946000
H	0.181319000	0.115387000	-4.139726000

H	-0.048310000	-2.349349000	-0.963578000
H	0.189088000	2.047164000	-2.792141000
C	0.069138000	2.159077000	-0.039466000
H	-0.834392000	2.180120000	0.579275000
H	0.918656000	2.124485000	0.651179000
H	0.122797000	3.086450000	-0.618362000

24dtT_$^{1}n_{8}\pi_{8}$*

N	0.130937000	-0.029926000	-3.132042000
C	0.065088000	-1.316769000	-2.696389000
N	-0.000635000	-1.438515000	-1.325314000
C	-0.002588000	-0.363012000	-0.424215000
C	0.065383000	0.929273000	-0.921631000
C	0.133362000	1.093934000	-2.304505000
S	0.063777000	-2.643410000	-3.712129000
S	-0.093608000	-0.805886000	1.284760000
H	0.179974000	0.077880000	-4.136106000
H	-0.048404000	-2.390375000	-0.987986000
H	0.189197000	2.052802000	-2.798426000
C	0.066160000	2.119428000	0.002179000
H	-0.843570000	2.149607000	0.614587000
H	0.922980000	2.092798000	0.686848000
H	0.119318000	3.054401000	-0.562699000

24dtT_$^{1}\pi_{7}\pi_{8}$*

N	0.132205000	-0.031058000	-3.154912000
C	0.065937000	-1.244782000	-2.650144000
N	0.001794000	-1.416230000	-1.360421000
C	-0.004403000	-0.321801000	-0.346785000
C	0.067145000	0.960515000	-0.938523000
C	0.134788000	1.141921000	-2.301689000
S	0.064603000	-2.674479000	-3.759566000
S	-0.091907000	-0.801552000	1.264362000
H	0.180171000	0.065605000	-4.158031000
H	-0.048192000	-2.355434000	-0.981010000
H	0.192082000	2.086767000	-2.817081000
C	0.069283000	2.163998000	-0.038986000
H	-0.833555000	2.171975000	0.581263000
H	0.916893000	2.115735000	0.653286000
H	0.123011000	3.094581000	-0.611668000

24dtT_$^{3}\pi_{8}\pi_{8}$*

C	-0.678646000	-1.371557000	-0.052004000
C	-1.026791000	-0.044737000	0.075707000
C	1.345487000	0.666382000	-0.003533000
C	0.715093000	-1.695036000	-0.158260000
H	1.095515000	-2.700200000	-0.261498000

N	0.007337000	0.920920000	0.094551000
H	-0.258238000	1.892618000	0.188157000
N	1.642857000	-0.669058000	-0.128474000
H	2.631800000	-0.872563000	-0.202902000
S	-2.658770000	0.602200000	0.221817000
S	2.527021000	1.845722000	0.022968000
C	-1.663262000	-2.503811000	-0.087735000
H	-2.688535000	-2.145028000	0.003583000
H	-1.568256000	-3.063727000	-1.027133000
H	-1.462993000	-3.210573000	0.727927000

24dtT_$^{3}n_{8}\pi_{8}$*

N	0.130995000	-0.030711000	-3.130938000
C	0.065419000	-1.318999000	-2.694813000
N	-0.000746000	-1.444274000	-1.328229000
C	-0.002622000	-0.368861000	-0.420196000
C	0.065251000	0.928701000	-0.921222000
C	0.132358000	1.092766000	-2.296109000
S	0.064118000	-2.642191000	-3.716575000
S	-0.091460000	-0.796190000	1.284768000
H	0.179934000	0.079503000	-4.134210000
H	-0.049089000	-2.398026000	-0.997034000
H	0.187800000	2.052969000	-2.787762000
C	0.066200000	2.121539000	0.000127000
H	-0.844467000	2.155457000	0.610886000
H	0.922148000	2.096265000	0.685886000
H	0.121533000	3.054280000	-0.567649000