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

Supporting Information

Unexpected Longer T_1 Lifetime of 6-Sulfur Guanine than 6-Selenium Guanine: Solvent Effect from Hydrogen Bond to Brake the Triplet Decay

Shaoting Liu, Yuhsuan Lee, Lingfang Chen, Jingheng Deng, Tongmei Ma, Mario Barbatti, and Shuming Bai

Table of Contents

S1. Cartesian coordinates for all optimized structures

Table S1. 6tGua optimized structures using ADC(2)/aug-cc-pVDZ calculation.

S_0 min

C	-0.4507531	0.8810128	0.0352625
C	-0.1982678	3.3065186	0.2730578
C	-2.3400534	2.0471077	0.0408862
H	-2.0939775	4.0843526	0.3291815
C	0.3930395	2.0006511	0.1771875
N	0.3974698	-0.1997763	-0.0180463
H	0.1160378	-1.1693587	-0.1188009
N	1.722748	1.6219643	0.2119004
C	1.6838414	0.2948482	0.0924405
N	-1.8135848	0.8405696	-0.0572707
N	-1.6048157	3.1979132	0.2052144
N	-3.7218007	2.2006158	0.0527618
H	-4.0746003	3.0160963	-0.4409767
H	-4.1903397	1.3442412	-0.2311109
S	0.5248627	4.7888275	0.4546429
H	2.5532051	-0.3589144	0.0803652

T_1 op-S

C	-0.4424699	0.9036115	0.0006991
C	-0.2183324	3.2976729	0.5634534
C	-2.3445699	2.07236	0.0608543
H	-2.1744649	4.0576273	0.5066445
C	0.3920034	2.0068967	0.3250788
N	0.4097293	-0.1717504	-0.0957827
H	0.1371924	-1.1248936	-0.3118549
N	1.711015	1.6134977	0.4084678
C	1.6833551	0.3000928	0.1484464
N	-1.8007784	0.8694592	-0.1375437
N	-1.6462671	3.2042232	0.3411301
N	-3.7296682	2.1724585	0.038344
H	-4.1051805	3.0395838	-0.3350347
H	-4.1564889	1.3476854	-0.374286
S	0.6332264	4.658854	-0.1777995
H	2.5547063	-0.3507017	0.1258786

T_1 ring-distorted

N	-1.5595773	3.2591188	-0.096388
C	-0.2459908	3.3021309	0.2831779
C	0.389001	2.0105774	0.2107092
C	-0.4923309	0.8458721	0.0500368
N	-1.746314	0.8280438	-0.2940255
C	-2.1402357	2.1449182	-0.7765287

N	1.6452968	1.6304167	0.6134647
C	1.5710952	0.3001859	0.7107481
N	0.3210217	-0.2183406	0.4336119
S	0.4865253	4.6849319	0.8940544
N	-3.542172	2.269165	-0.9661856
H	-2.1078172	4.1132822	0.0127301
H	0.0569764	-1.1977245	0.4100224
H	-3.7736533	2.8119041	-1.7982726
H	-3.9491896	1.3379521	-1.0536572
H	2.408663	-0.3410968	0.9814223

Table S2. 6SeGua optimized structures using ADC(2)/aug-cc-pVDZ calculation.

		S_0 min	
Se	-0.1222025	3.1785054	-0.4484277
N	2.2948068	-1.3053889	0.199041
C	3.1545222	-0.2321651	0.0529493
N	2.5178995	0.9262696	-0.1190207
C	1.017042	-0.8046191	0.1161984
N	-0.1391115	-1.5280093	0.1874173
C	-1.2029000	-0.7518094	0.0812007
N	-2.4746416	-1.2960114	0.2129346
N	-1.1468174	0.6115822	-0.0880474
C	0.0110062	1.4034939	-0.2030675
C	1.1792909	0.5821888	-0.0817163
H	2.5421685	-2.2795728	0.3387745
H	-3.1861456	-0.8997735	-0.3950956
H	-2.4522953	-2.311461	0.1748824
H	-2.0175058	1.143125	-0.1076999
H	4.2353724	-0.3531724	0.0804929
		T_1 op-Se	
Se	-0.089145	3.0351126	-1.0082221
N	2.3035283	-1.3008027	0.1547335
C	3.1643741	-0.2317928	0.0783977
N	2.5206904	0.9456643	0.0092268
C	1.0200759	-0.787965	0.1319794
N	-0.1583494	-1.5179167	0.1065292
C	-1.212056	-0.7350618	0.0772724
N	-2.4957951	-1.2828512	0.166674
N	-1.1863357	0.6494537	0.0241802
C	0.0126771	1.4328481	0.0286813
C	1.1861722	0.5984086	0.0459707
H	2.5509232	-2.2829625	0.2120493
H	-3.1528531	-0.9046878	-0.5124958
H	-2.4499639	-2.2978597	0.1109792

H	-2.048544	1.1180577	0.2951702
H	4.2451297	-0.3544639	0.0796901

T_1 ring-distorted

Se	0.7631509	4.8710611	0.5641806
N	0.3252088	-0.160431	0.6169168
C	1.6260342	0.3286434	0.5993516
N	1.7190193	1.6344518	0.3774784
C	-0.5249007	0.9001592	0.3217616
N	-1.8232126	0.9040021	0.243529
C	-2.3280623	2.1885516	-0.2002925
N	-3.7215226	2.4373793	-0.0151531
N	-1.5382695	3.3245291	0.1625002
C	-0.1810517	3.3161427	0.2570891
C	0.4044879	2.0377198	0.2015265
H	0.0381399	-1.1267378	0.7309243
H	-4.2384415	2.2576192	-0.8750238
H	-4.096196	1.8080386	0.7007462
H	-2.029453	4.2154027	0.2498889
H	2.48029	-0.3292211	0.7544599

Table S3. T_1/S_0 crossing point structures of 6tGua.

DFT/B3LYP/cc-pVDZ

C	0.73791411	-0.99509572	-0.12990482
C	-0.45211516	1.10557541	0.47043926
C	-1.47855206	-1.14379822	0.03413706
H	-2.45219304	0.50309983	0.72633733
C	0.79788356	0.37589739	0.25502849
N	2.04387021	-1.39494515	-0.22520227
H	2.36381961	-2.32617019	-0.46119536
N	2.11233663	0.77153116	0.39558642
C	2.82101213	-0.29243857	0.10211002
N	-0.34692392	-1.77619389	-0.29369787
N	-1.54128233	0.12525154	0.48864225
N	-2.64022724	-1.86840511	-0.02419788
H	-3.49807774	-1.36417665	-0.21998631
H	-2.54340689	-2.75203068	-0.51373114
S	-0.42932053	2.18366051	-0.97759745
H	3.90826281	-0.34546164	0.10838227

DFT/B3LYP/cc-pVDZ PCM (water)

C	0.78359900	-0.96820093	-0.13614930
C	-0.51154018	1.10689881	0.38506661
C	-1.43952327	-1.19408481	0.01797613
H	-2.48954636	0.42432942	0.64091523
C	0.78446425	0.42110880	0.21689790

N	2.10972884	-1.31834366	-0.17749855
H	2.48623321	-2.23623450	-0.38990939
N	2.07098318	0.86270642	0.39515546
C	2.83176652	-0.19110375	0.14342254
N	-0.25986103	-1.79169087	-0.27656979
N	-1.55324313	0.07593226	0.46288984
N	-2.54734899	-1.94235058	-0.11965561
H	-3.45829979	-1.60296776	0.16290121
H	-2.43577851	-2.93127558	0.30817027
S	-0.54712987	2.10022468	-1.10608797
H	3.91936606	-0.20622783	0.17688601

TDA/B3LYP/cc-pVDZ

C	0.73634631	-0.99653338	-0.12672784
C	-0.45154061	1.10646212	0.47025235
C	-1.47857102	-1.14373559	0.02570240
H	-2.44659120	0.48767264	0.74284481
C	0.79311187	0.37746011	0.25006749
N	2.04070883	-1.39785884	-0.21103560
H	2.35753209	-2.32818045	-0.45361085
N	2.11104614	0.77580179	0.38369653
C	2.81806253	-0.29015678	0.10210354
N	-0.34741699	-1.77873798	-0.29836235
N	-1.53912642	0.12807937	0.46808406
N	-2.64084694	-1.86894555	-0.02267378
H	-3.50321141	-1.37110819	-0.21722450
H	-2.54089504	-2.75179918	-0.51230580
S	-0.41052729	2.20146330	-0.96952203
H	3.90490913	-0.34359343	0.10386156

TDA/B3LYP/cc-pVDZ PCM (water)

C	0.78043642	-0.96543927	-0.13780835
C	-0.50979629	1.10626379	0.39257564
C	-1.43985161	-1.19384338	0.01402650
H	-2.48677717	0.42027254	0.65455366
C	0.77830490	0.42431408	0.21836896
N	2.10551438	-1.31644643	-0.17871917
H	2.47942432	-2.23763686	-0.38191320
N	2.07026664	0.86627436	0.38916447
C	2.82691241	-0.18749725	0.14007559
N	-0.26147099	-1.78945537	-0.28332735
N	-1.55146903	0.07846244	0.45963958
N	-2.54793506	-1.94291520	-0.12301585
H	-3.45898702	-1.60863888	0.16483335
H	-2.43181234	-2.93174806	-0.30865018
S	-0.52308409	2.09033977	-1.10929197

H	3.91419455	-0.20357627	0.17756830

Table S4. T_1/S_0 crossing point structures of 6SeGua.

DFT/B3LYP/cc-pVDZ

Se	1.90970030	-0.20291376	-0.81408116
N	-2.41510044	-1.54800780	-0.28180628
C	-1.59287623	-2.60362600	0.08418030
N	-0.39597313	-2.21748803	0.45653446
C	-1.67448098	-0.40486319	-0.13629464
N	-2.11458459	0.86000174	-0.33105617
C	-1.21244287	1.76483253	0.03899859
N	-1.56580480	3.09184271	-0.04125417
N	0.00165001	1.46802442	0.55908930
C	0.61948762	0.15294065	0.64506607
C	-0.40572126	-0.84135862	0.32474894
H	-3.37714389	-1.59176755	-0.59515760
H	-0.82657433	3.75485428	-0.25344575
H	-2.41169403	3.23673188	-0.58382268
H	0.58874791	2.24042043	0.85126341
H	-1.93658935	-3.63565378	0.04649743

DFT/B3LYP/cc-pVDZ PCM (water)

Se	1.84098592	-0.10464727	-0.88407849
N	-2.36199755	-1.60075096	-0.29793611
C	-1.54574755	-2.62704818	0.12445137
N	-0.35137403	-2.21481911	0.51004511
C	-1.63916497	-0.44048683	-0.17949252
N	-2.09885759	0.80645666	-0.38224801
C	-1.22800971	1.74731305	0.02344857
N	-1.59842308	3.03608086	-0.11245286
N	-0.03295432	1.47477775	0.61472023
C	0.63241556	0.18357766	0.62049812
C	-0.36909731	-0.85057641	0.32095525
H	-3.32106208	-1.68436935	-0.61923033
H	-0.94559068	3.79768176	0.02290807
H	-2.46976717	3.22824494	-0.59220534
H	0.54148611	2.26695558	0.88352078
H	-1.88449162	-3.66128001	0.12314601

TDA/B3LYP/cc-pVDZ

Se	2.01608490	-0.16864687	-0.67485550
N	2.37604318	-1.60556309	-0.28974219
C	-1.51280223	-2.63474026	0.06432543
N	-0.33543618	-2.21076811	0.44674485
C	-1.68115004	-0.43987756	-0.12388231
N	-2.15605731	0.80743350	-0.33633728

C	-1.28213656	1.73609219	0.03698172
N	-1.66426649	3.05479052	-0.05025557
N	-0.06044580	1.46849303	0.56309400
C	0.56758239	0.17970204	0.72128175
C	-0.40032619	-0.82722142	0.34850991
H	-3.33016371	-1.68455364	-0.62082590
H	-0.93432821	3.72781156	-0.26223235
H	-2.50638901	3.17917969	-0.60409478
H	0.46894493	2.25754541	0.91758115
H	-1.82301729	-3.67704705	0.01594699
	TDA/B3LYP/cc-pVDZ	PCM (water)	
Se	1.87221051	-0.15560408	-0.79618445
N	-2.37585205	-1.57875899	-0.32509560
C	-1.57307856	-2.61378646	0.10630914
N	-0.38505282	-2.21651801	0.51512061
C	-1.64730171	-0.42650868	-0.18594279
N	-2.08708712	0.82256137	-0.40949228
C	-1.21491027	1.75440297	0.01375979
N	-1.57079836	3.04775209	-0.12599451
N	-0.03495176	1.46508236	0.62344382
C	0.60722940	0.16790141	0.69323890
C	-0.38876266	-0.84451264	0.34230351
H	-3.33133277	-1.65220846	-0.65906275
H	-0.90444292	3.79872939	0.00370397
H	-2.41566749	3.24493025	-0.64855795
H	0.53149090	2.25017365	0.92770177
H	-1.92516233	-3.64366616	0.09723883

Table S5. T_1/S_0 crossing point structures of 6tGua mono-hydrated complex.

	DFT/B3LYP/cc-pVDZ	PCM (water)	
C	1.50323607	0.61312740	-0.12874287
C	-0.46882469	-0.76169338	0.56679891
C	-0.44982162	1.68666343	0.06796077
H	-2.05275522	0.60129851	0.69548934
C	0.98237431	-0.64863261	0.31565469
N	2.85919139	0.41523896	-0.22744438
H	3.55125054	1.10676983	-0.49751551
N	2.00143204	-1.54548857	0.48452071
C	3.10047528	-0.88670954	0.14048954
N	0.86076160	1.77264339	-0.27758255
N	-1.02698942	0.59838373	0.62611800
N	-1.19134161	2.78877192	-0.13578248
H	-2.15037703	2.85314765	0.18088933
H	-0.71763465	3.63393609	-0.43198916

S	-0.96204690	-1.68907015	-0.88562837
H	4.10589480	-1.30267238	0.13660557
O	-3.72894624	-0.14031186	0.13957429
H	-3.94482111	-0.80745539	0.81195500
H	-3.19349758	-0.64959708	-0.50312082
	TDA/B3LYP/cc-pVDZ	PCM (water)	
C	1.50153795	0.61364019	-0.13021431
C	-0.46785448	-0.76321758	0.57541951
C	-0.44992123	1.68685581	0.06710496
H	-2.04994119	0.60202224	0.69797320
C	0.97714216	-0.64931845	0.31243261
N	2.85757820	0.41574773	-0.22650257
H	3.55095952	1.10626656	-0.49582268
N	1.99942437	-1.54774799	0.47883241
C	3.09609909	-0.88696219	0.13986870
N	0.86155367	1.77347997	-0.27677352
N	-1.02518090	0.59707855	0.62034268
N	-1.19124291	2.78900102	-0.13569288
H	-2.15020626	2.85239317	0.18100083
H	-0.71763907	3.63390457	-0.43280182
S	-0.94815555	-1.68894732	-0.88925995
H	4.10260635	-1.30037044	0.13973367
O	-3.72532659	-0.13888013	0.14289271
H	-3.95010613	-0.80724426	0.81101099
H	-3.19377699	-0.64935141	-0.50129453

Table S6. T_1/S_0 crossing point structures of 6SeGua mono-hydrated complex.

	DFT/B3LYP/cc-pVDZ	PCM (water)	
Se	0.30678513	-1.79528758	-0.96184184
N	-2.90806460	1.26045443	-0.18865297
C	-3.41469193	0.06753750	0.27659701
N	-2.47497559	-0.80295950	0.60079667
C	-1.53890980	1.15012608	-0.16970327
N	-0.66368808	2.13708926	-0.42730067
C	0.59976393	1.79338400	-0.10128927
N	1.57439357	2.69443223	-0.31158852
N	0.95083788	0.60897423	0.47297893
C	0.11351465	-0.57145132	0.54726943
C	-1.28604915	-0.16456412	0.32173088
H	-3.44347576	2.07817014	-0.46108156
H	2.54433335	2.45618547	-0.10333488
H	1.32449656	3.59249573	-0.70531264
H	1.95441359	0.47744779	0.61865435
H	-4.48689600	-0.10471794	0.35019296

O	3.83684294	1.09640472	0.43891975
H	4.39083381	0.70359895	-0.25498971
H	4.42119534	1.14003005	1.21266527

TDA/B3LYP/cc-pVDZ PCM (water)

Se	0.78032081	-1.89930996	-0.81545322
N	-3.27920925	-0.06792534	-0.17122121
C	-3.33249742	-1.32278151	0.39679736
N	-2.15014277	-1.78396094	0.75242318
C	-1.95969834	0.30852541	-0.18511323
N	-1.48514518	1.50667456	-0.55628119
C	-0.17773099	1.64900548	-0.25433358
N	0.42378547	2.80628190	-0.58047960
N	0.56444508	0.70626436	0.38642332
C	0.18862385	-0.66886129	0.62257887
C	-1.25580766	-0.79071070	0.39565874
H	-4.06606201	0.48649488	-0.49219970
H	1.39977966	2.96091458	-0.32985986
H	-0.14783337	3.55499207	-0.95057944
H	1.54057347	0.96010932	0.55443276
H	-4.27835323	-1.84636167	0.52345129
O	3.05659335	2.20655036	0.40034024
H	3.48840325	2.50946853	1.21504347
H	3.79031528	1.90949995	-0.16172820

S2. Parameters used in the quasi-Marcus formula

The classic Marcus formula can be expressed as:[1, 2]

$$k_{ISC} = \frac{2\pi}{\hbar}|H_{SOC}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} exp\left(-\frac{(\lambda + \Delta G^0)^2}{k_B T}\right) \quad (1)$$

where ΔG^0 is the total Gibbs free energy variation for the electron transfer. The quasi-Marcus formula is an approximation of classic Marcus formula and parameters used in it are shown in Figure S1:

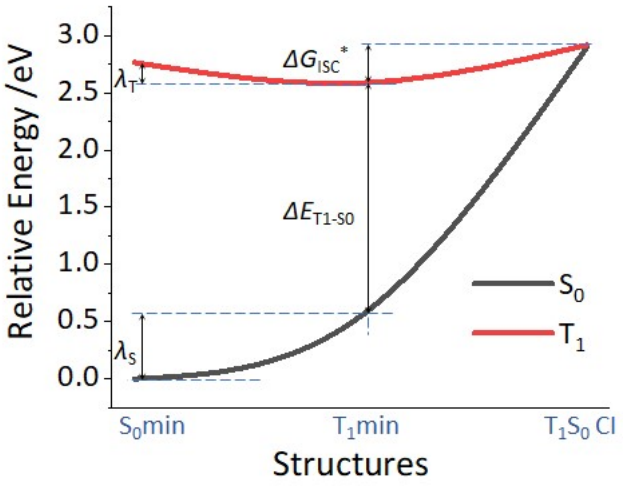
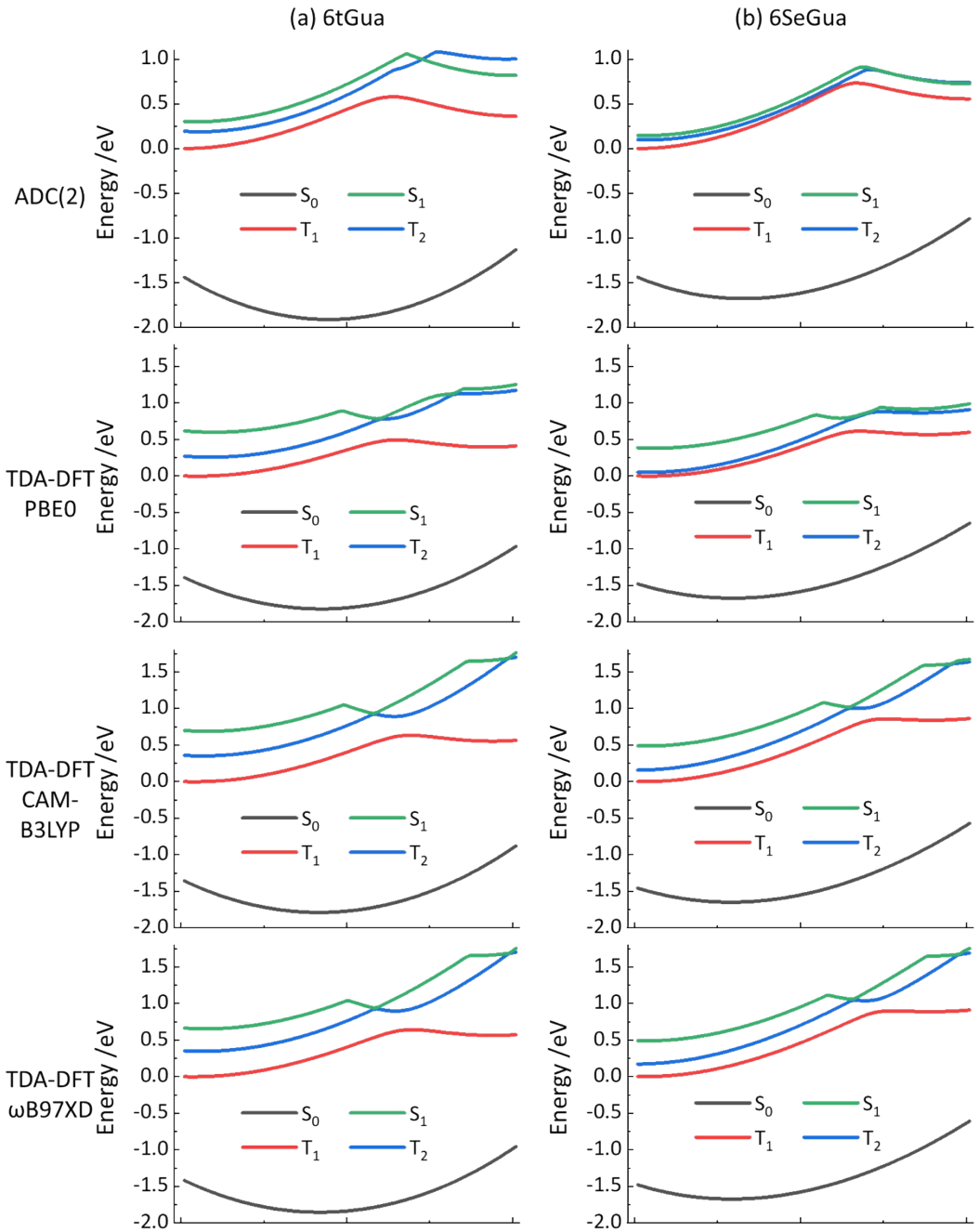


Figure S1. Definition of parameters used in the quasi-Marcus equation with the energy profiles between S_0 minimum structure and T_1/S_0 crossing point.

The reorganization energy (λ) includes two distinct components. λ_S is the S_0 energy difference between the T_1 and the S_0 minimum geometries, while λ_T is computed as the T_1 energy difference between corresponding structures. The activation energy (ΔG_{ISC}^*) is the T_1 Gibbs free energy difference between the initial T1 minimum and the final T_1/S_0 crossing point during the triplet decay process. $\Delta E_{T1\text{-}S0}$ is the energy difference between the T_1 and ground states at the T_1-optimized structure.

1. R. A. Marcus, *The Journal of Chemical Physics*, 1984, **81**, 4494-4500.
2. Q. Ou and J. E. Subotnik, *The Journal of Physical Chemistry C*, 2013, **117**, 19839-19849.

S3. Potential energy profiles of 6tGua and 6SeGua computed at different levels



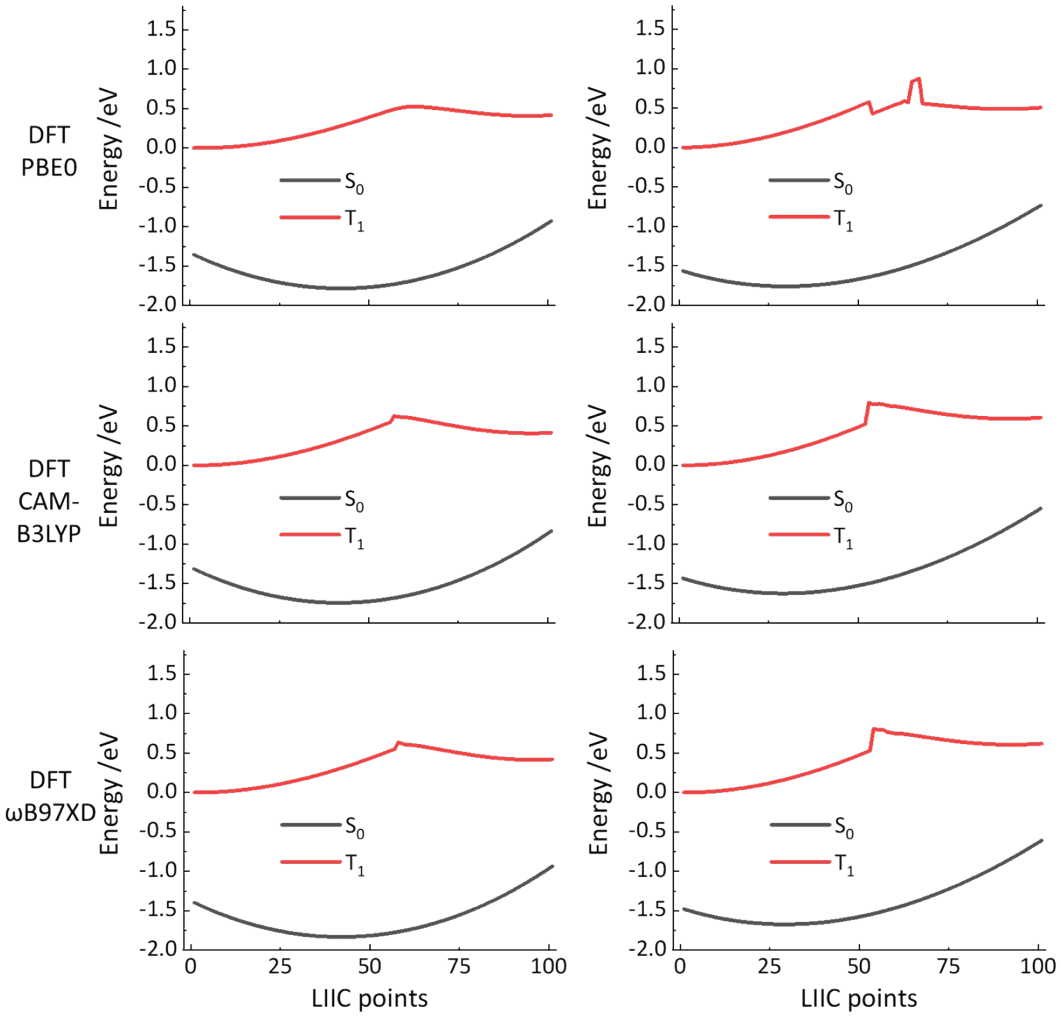


Figure S2. Potential energy profiles for the lowest excited states for (a) 6tGua and (b) 6SeGua from ADC(2), TDA-DFT, and DFT calculations with different functionals.

S4. The reorganization energy of 6tGua and 6SeGua in gas phase and with solvent model

Table S7. The reorganization energy of 6tGua and 6SeGua computed at DFT/B3LYP and TDA-DFT/B3LYP level.

	DFT/B3LYP			TDA-DFT/B3LYP		
λ/eV	Gas phase	Implicit solvent	mono-hydrated[a]	Gas phase	Implicit solvent	mono-hydrated[a]
6tGua	0.53	0.31	0.32	0.47	0.19	0.21
6SeGua	0.68	0.72	0.68	0.56	0.65	0.61

[a]mono-hydrated complex same as the one in Figure 6 and Table 2.

S5. The Spin-orbit couplings of 6tGua and 6SeGua

Table S8. The Spin-orbit couplings of 6tGua and 6SeGua computed at the two optimized T_1 structures as shown in Figure 2.

T_1 optimized structure	Op-S/Se	Ring distorted
SOCs /cm^{-1}	TDA-B3LYP	TDA-B3LYP
6tGua	82.1	15.8
6SeGua	611.0	93.0

Table S9. The Spin-orbit couplings of 6tGua and 6SeGua computed at the TD-B3LYP level, with the same structures as calculated in Table 1.

T_1/S_0 crossing	B3LYP		TDA-B3LYP	
SOCs /cm^{-1}	gas phase	PCM	gas phase	PCM
6tGua	89.8	74.7	90.3	76.0
6SeGua	474.6	408.5	520.7	427.2
SOC Ratio	5.3	5.5	5.8	5.6

S6. Mono-hydrated complex of 6tGua and 6SeGua

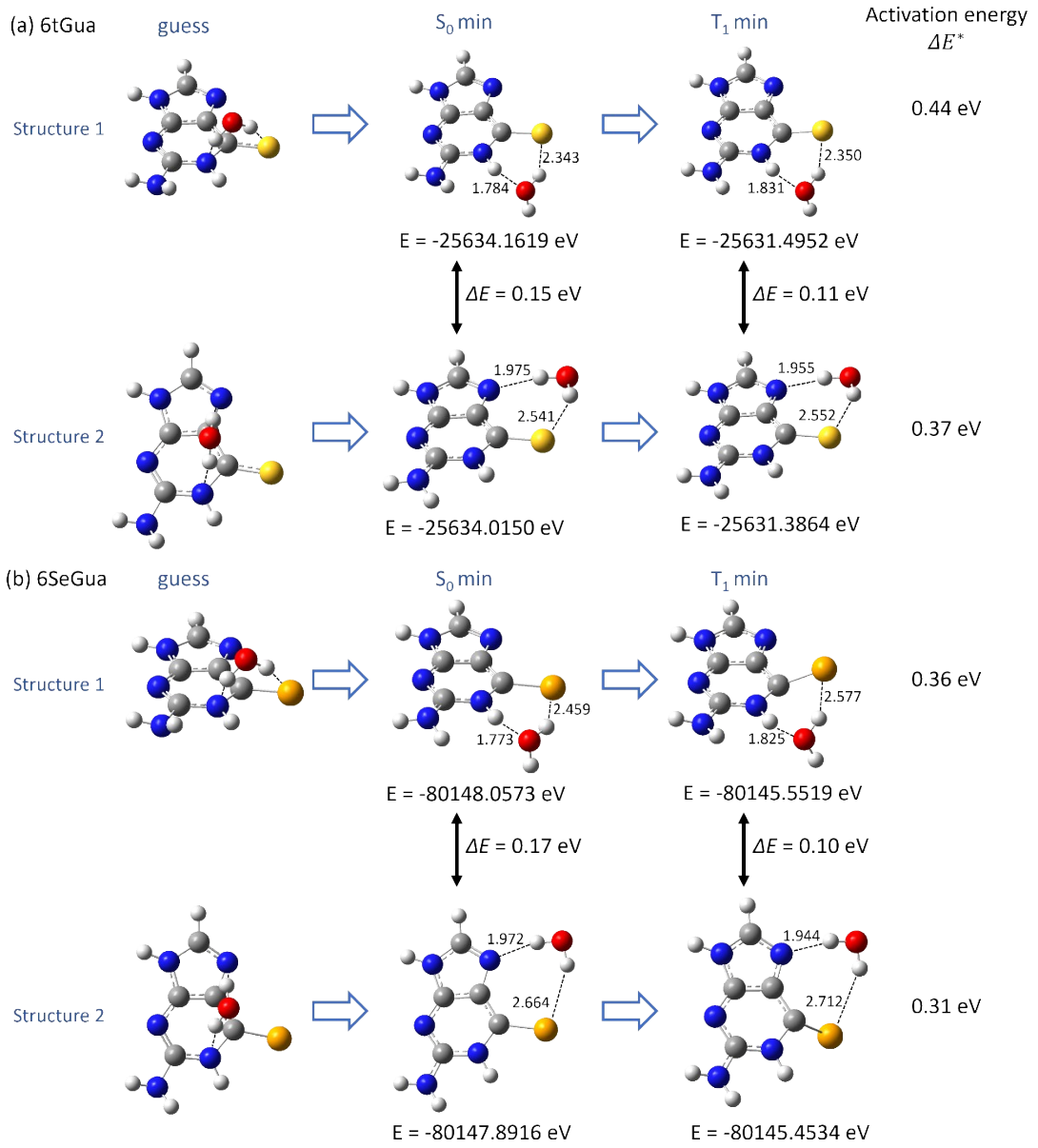


Figure S3. The different structures forming a mono-hydrated complex of (a) 6tGua and (b) 6SeGua at B3LYP/cc-pVDZ level. Bond length unit: Å.

S7. Di-hydrated complex and tri-hydrated complex of 6tGua and 6SeGua

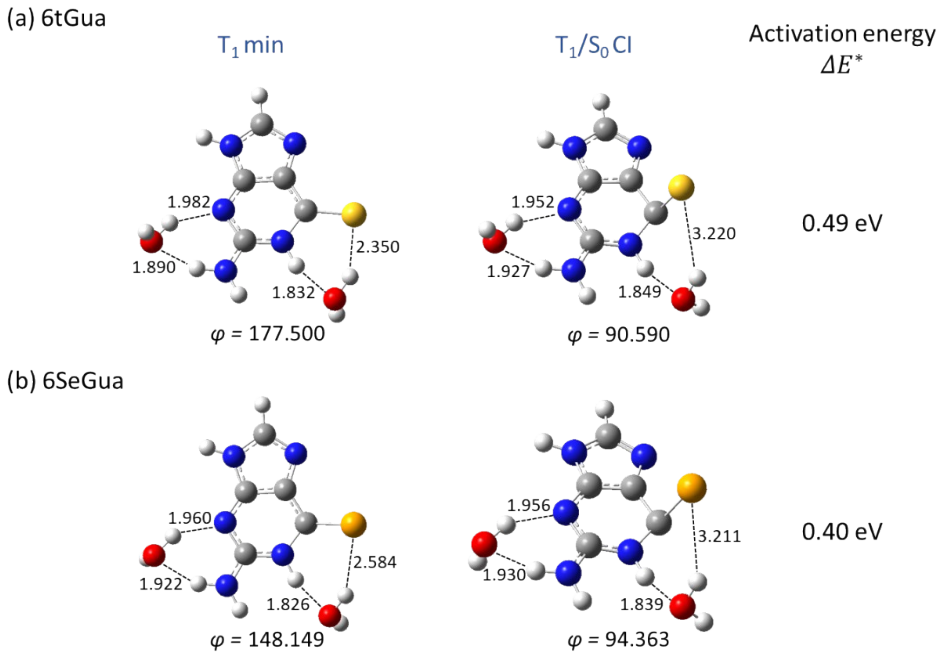


Figure S4. The optimized structure of di-hydrated complex of (a) 6tGua and (b) 6SeGua at TDA-B3LYP/cc-pVDZ level. Bond length unit: Å.

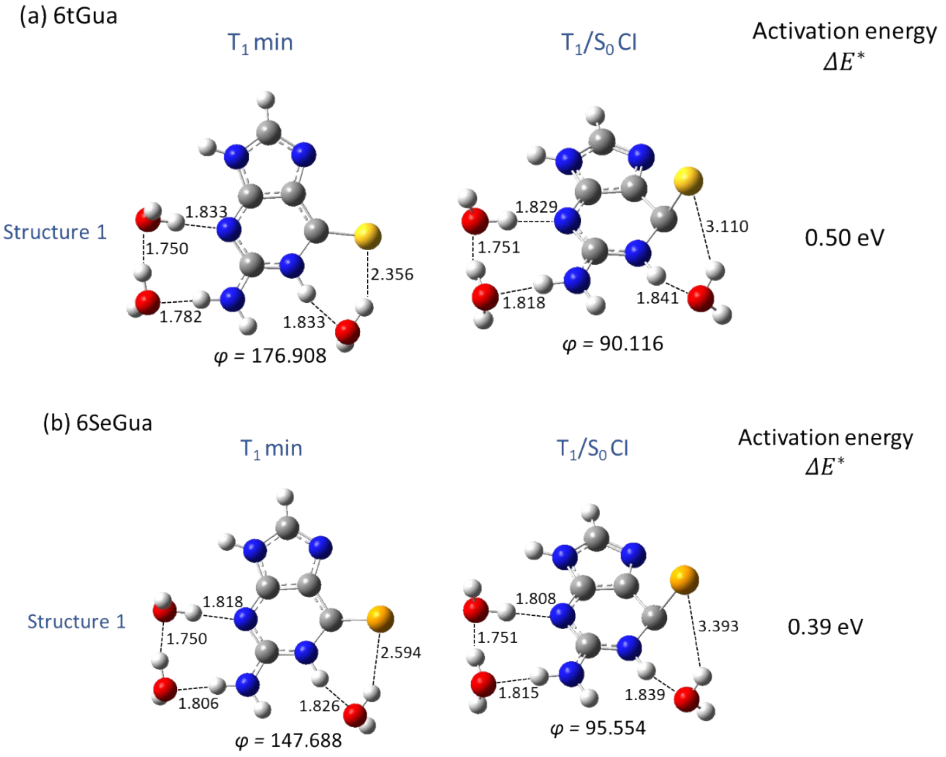


Figure S5. The optimized structure of tri-hydrated complex of (a) 6tGua and (b) 6SeGua at TDA-B3LYP/cc-pVDZ level. Bond length unit: Å.