Supplementary information:

Optical Absorption and Magnetic Circular Dichroism spectra of thiouracils: a quantum mechanical study in solution

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1. Comparison of the computed energies for thiouracils with other values reported in the literature and experimental values.

Table S1. Effect of the thionation on the position of the lowest energy bright transition.

	CAMB3LYP			B3LYP			Exp. Uracil	CASPT2 Thymine	Exp. Thymine
	GP 6-31G(d)	GP aug-cc-pvtz	PCM+4H_2O aug-cc-pvtz	GP 6-31G(d)	GP- aug-cc-pvtz	PCM+4H_2O aug-cc-pvtz	ref[1]	ref[2]	ref[3]
U	5.70(0.17)	5.45 (0.17)	5.26 (0.24)	5.42(0.11)	5.21(0.12)	5.06 (0.18)	4.77	5.02	4.64
2T-U	4.82 (0.18) [-0.88]	4.62 (0.20) [-0.83]	4.64 (0.27) [-0.62]	4.18 (0.05) [-1.24]	4.07 (0.05) [-1.14]	4.20 (0.08) [-0.86]	4.27 [-0.50]	[-0.69]	[-0.38]
4T-U	4.52 (0.39) [-1.18]	4.34 (0.42) [-1.11]	4.20 (0.47) [-1.06]	4.34 (0.28) [-1.08]	4.17 (0.24) [-1.04]	4.08 (0.40) [-0.98]	3.76 [-1.01]	[-1.02]	[-0.92]
2,4-DTU	4.20 (0.10) [-1.50]	4.08 (0.27) [-1.37]	4.04 (0.29) [-1.22]	3.61 (0.01) [-1.81]	3.55 (0.01) [-1.66]	3.62 (0.06) [-1.44]	3.44 [-1.33]	[-1.30]	[-1.26]

Table S2. Effect of the thionation on the energy gap between the lowest energy bright transition and the lowest energy dark transition

	CAMB3LYP		B3LYP		CASPT2 Thymine
	GP aug-cc-pvtz	PCM+4H_2O aug-cc-pvtz	GP aug-cc-pvtz	PCM+4H_2O aug-cc-pvtz	
U	0.34		0.49		0.25[4]
2T-U	0.76	0.42	0.5	0.32	0.5[5]
4T-U	1.3	0.66	1.38	0.84	1.1[6]
2,4-DTU	1.0	0.50	0.79	0.43	

2. Further details for the calculated spectra

a) Conversion from molar ellipticity to molar extinction coefficient anisotropy

The molar ellipticity $[\vartheta]_M$ (in standard units [deg M^{-1} cm^{-1} T^{-1}]) can be converted into extinction coefficient anisotropy $\Delta\varepsilon$ (in stardard units [M^{-1} cm^{-1} T^{-1}]) according to[7]

$$\Delta\varepsilon = [\vartheta]_M/3298$$

b) MCD units in the literature

MCD spectra have been reported in the literature in several different units. The only paper we are aware of

that reports MCD of nucleobases directly as extinction coefficient anisotropy Δε in the standard units M^{-1} cm^{-1} T^{-1} was published by Sutherland and Griffin.[8] For adenine in water at pH 7, the lowest energy peak of the MCD spectrum was found at 270 nm and had value ~ -1.6 M^{-1} cm^{-1} T^{-1}, which is in good agreement with what we computed, adopting exactly the same methodology used here, in Ref. [9], namely -2.5 M^{-1} cm^{-1} T^{-1}.

In an older paper dated 1968, Voelter *et al.*[10] reported the MCD of several nucleobases and nucleotides, including adenine, adenosine, uracil and uridine, as 10^{-3} $[\vartheta]_{M,}$ where the molar ellipticity $[\vartheta]_M$ was nominally expressed in deg mol^{-1} cm^2. For adenine at 270 nm, the value reported by Voelter *et al.* was thus $[\vartheta]_M$ =-27500 at 49.5 kG. However, when translated into Δε in standard units, the 270 nm MCD peak of adenine is apparently found at -1.68 x 10^{-3} M^{-1} cm^{-1} T^{-1}, versus the value -1.6 M^{-1} cm^{-1} T^{-1} M^{-1} reported by Sutherland and Griffin. Therefore -as we also did in Refs. [9] and [11]- we assume here that Voelter *et al.* misprinted the units, and that the values they report must be multiplied by a factor 10^3 or, in other words, that they were already reporting $[\vartheta]_M$ in standard units.

c) The MCD units of Ref. [12]

In the present investigation, experimental spectra were taken from Ref. [12], where it is written that MCD spectra are given as molar ellipticity $[\vartheta]_M$ in units of deg M^{-1} m^{-1} T^{-1}, once again different from standard units. To obtain the molar ellipticity $[\vartheta]_M$ in standard units, one has to divide the results by 10^2. Then, to further convert $[\vartheta]_M$ into Δε, one has to divide by the factor 3298. So, all in all, to convert the experimental molar ellipticity $[\vartheta]_M$ taken from Ref [12] in the given units , into the anisotropy Δε in standard units (M^{-1} cm^{-1} $T^{-1)}$, we should divide them by 3.298 10^5. This, however, yields MCD intensities that are about 10^6 times smaller than the computed ones (see below). This is a strange finding since this problem does not show up for OPA intensities (as reported in the manuscript, although generally overestimated, computed values are within a factor 4 from the experiment). Therefore we hypothesize that the units of the MCD data in Ref. [12] were misprinted.

Unfortunately we could not find any other MCD data for thiouracils in literature for direct comparison. However, the existence of a misprint of the MCD units in Ref. [12] is documented by a comparison with the MCD peak at 260 nm of uridine in water (pH=7). In Table I of Ref. [12], the MCD peak is reported to be -1.8 10^{-1} deg M^{-1} m^{-1} T^{-1} = -1.8 10^{-3} deg M^{-1} cm^{-1} T^{-1}. On the contrary, in Table I of Voelter *et al.*[10] (from where we actually suppose the value given in Tab I of Ref. [12] was taken, since the reference cited therein does not contain any MCD data) it has a value of -9.0 10^3 deg mol^{-1} cm^2 for a field of 49.5 kG, corresponding to -1.8 deg M^{-1} T^{-1}, a value 10^3 larger than the one reported in Ref. [12].
In synthesis, the MCD intensities reported in Ref. [12] (for uridine) are 10^3 smaller than those reported by Voelter *et al.*, and those reported by Voelter *et al.* (for adenine) are 10^3 smaller than those given by Sutherland and Griffin,[8] the latter being the only one reported directly in standard units. These considerations suggest that the values of the experimental MCD intensities of thiouracils reported in Ref. [12] should be multiplied by a factor 10^6. Figures S1-S2 actually show that after correcting the experimentally derived data by 10^6 (in practice this means that the original MCD intensities were multiplied by a factor 10^6/3.298 10^5), their order of magnitude is in agreement with the ones we computed.

Figure S1: The OPA and MCD spectra of 2-thiouracil (left lanels), 4-thiouracil (middle panels) and 2,4-di-thiouracil (right). Comparison of computed (TD-B3LYP/aug-cc-pVDZ) and experimental results. The experimental results from Ref. [12] have been transformed from molar ellipticity $[\vartheta]_M$ (in given units) into $\Delta\varepsilon$ (in standard units) and multiplied by a factor 10^6.

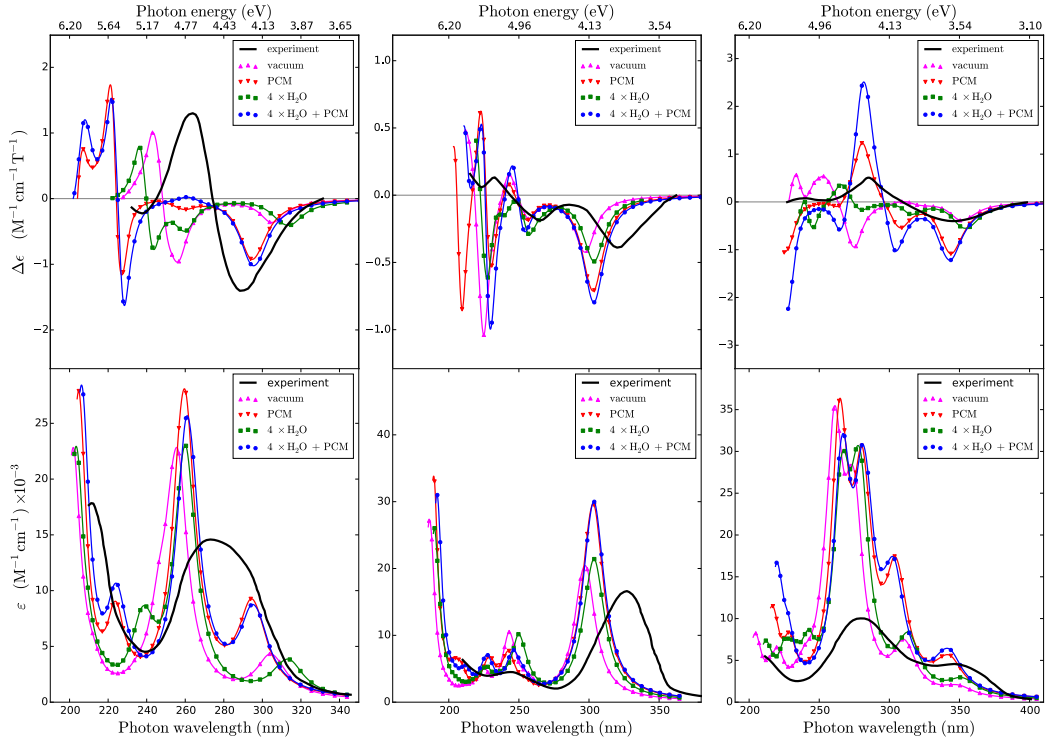

Figure S2: The OPA and MCD spectra of 2-thiouracil (left panels), 4-thiouracil (middle panels) and 2,4-dithiouracil (right panel). Comparison of computed (TD-CAM-B3LYP) and experimental results. The experimental results from Ref. [12] have been transformed from molar ellipticity $[\vartheta]_M$ (in given units) into $\Delta\varepsilon$ (in standard units) and multiplied by a factor 10^6.

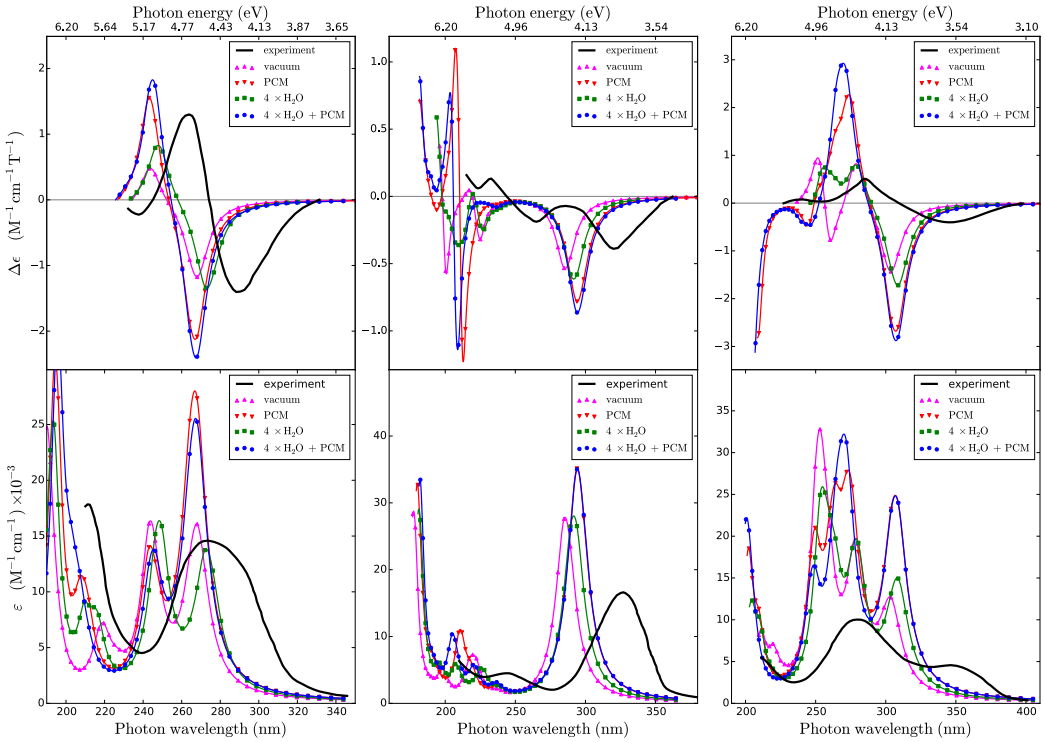

Table S3. XYZ Coordinates of the optimized ground state minima for the cluster thiouracil+4H_2O in PCM at the B3LYP/aug-cc-pvtz level of theory.

2-TU	X	Y	Z
N	0.301353	-0.405858	-0.160191
N	-1.930306	-0.884798	0.088675
C	-0.977777	0.051076	-0.148834
C	-1.640220	-2.200043	0.305969
C	-0.370668	-2.653219	0.300002
C	0.704675	-1.728304	0.056273
S	-1.371570	1.673771	-0.418586
O	1.897198	-2.029218	0.027047
O	2.506815	1.425305	-0.645170
O	-4.420070	0.460612	0.065519
O	1.293562	3.242563	1.177916
O	4.237282	-0.575888	-0.116644
H	1.044459	0.279456	-0.355316
H	-2.906567	-0.561820	0.097422
H	-2.492836	-2.838265	0.481979
H	-0.137000	-3.690094	0.472896
H	0.409746	2.950576	0.916509
H	3.458089	-1.163851	-0.037461
H	3.263787	0.814978	-0.477265
H	2.602755	1.738717	-1.550386
H	1.864496	2.710018	0.600144
H	-3.846449	1.218734	-0.135812
H	-4.946798	0.326507	-0.730562
H	4.619738	-0.534738	0.766038
4-TU	X	Y	Z
N	-0.077537	-0.247020	0.156586
N	2.119673	-0.951313	-0.083648
C	1.255886	0.097601	0.108113
C	1.697466	-2.234466	-0.217714
C	0.380747	-2.548235	-0.174682
C	-0.583259	-1.517339	0.018236
S	-2.239666	-1.823009	0.081833
O	1.649529	1.255169	0.230580
O	-1.791583	2.052588	0.665861
O	4.455548	0.655072	-0.033452
O	0.189230	3.654825	-0.619355
O	-4.048476	0.905997	-0.305152
H	-0.724630	0.534418	0.331585
H	3.111330	-0.697024	-0.110310
H	2.472103	-2.972371	-0.361375
H	0.050310	-3.566017	-0.286931
H	0.825246	2.955776	-0.412668
H	-3.590535	0.043922	-0.250738
H	-2.674879	1.780235	0.325018
H	-1.912364	2.241411	1.602407
H	-0.626768	3.296346	-0.236625
H	3.699331	1.243853	0.122991
H	4.952399	0.658648	0.791855
H	-4.180851	1.062697	-1.246679

2,4-DTU	X	Y	Z
N	0.139252	-0.323940	-0.130979
N	-2.074039	-0.927552	0.061827
C	-1.170411	0.060926	-0.161670
C	-1.712995	-2.215647	0.301842
C	-0.410565	-2.582043	0.332960
C	0.598330	-1.602178	0.106777
S	-1.646044	1.650050	-0.463330
S	2.238453	-1.972416	0.125535
O	2.001264	1.833597	-0.607121
O	-4.632754	0.237436	-0.054118
O	0.748295	3.366664	1.444109
O	4.352248	0.503312	-0.438740
H	0.831442	0.419644	-0.309467
H	-3.069188	-0.660108	0.039037
H	-2.524873	-2.908319	0.462672
H	-0.124445	-3.601609	0.524233
H	-0.129247	3.045963	1.201119
H	3.818461	-0.295172	-0.262582
H	2.923874	1.488625	-0.584221
H	1.880870	2.238863	-1.472352
H	1.313799	2.929654	0.785657
H	-4.129329	1.043718	-0.253204
H	-5.131279	0.047695	-0.857111
H	4.826311	0.674938	0.382505

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