Supporting Information

Natural and Magnetic Circular Dichroism Spectra of Nucleosides: Effect of the Dynamics and Environment

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Table S1. Nucleoside conformer relative free energies (*E*) and corresponding probabilities (*p*)

conformer	γ (deg.)	χ (deg.)	*E* (kcal/mol)	*p*
cytidine				
I	-117	59	0.75	0.22
II	56	52	0.00	0.77
III	-117	-63	4.41	0.00
IV	56	-63	3.02	0.00
V	-131	167	3.99	0.00
VI	63	167	3.42	0.00
uridine				
I	-117	52	6.72	0.00
II	63	52	3.00	0.01
III	160	-77	6.64	0.00
IV	63	-70	2.93	0.01
V	-160	-171	3.27	0.00
VI	63	-171	0.00	0.98
5-methyluridine				
I	-117	59	0.00	0.65
II	56	52	0.37	0.35
III	-124	-70	4.08	0.00
IV	63	-70	3.80	0.00
V	-117	167	3.11	0.00
VI	63	175	4.08	0.00
adenosine				
I	-117	59	0.81	0.20
II	63	59	0.00	0.79
III	-88	-63	4.42	0.00
IV	63	-70	4.20	0.00
V	-95	167	3.75	0.00
VI	63	175	2.96	0.01
guanosine				
I	-131	52	1.21	0.11
II	49	59	0.00	0.87
III	-95	-63	4.31	0.00
IV	56	-70	3.36	0.00
V	-95	-178	4.44	0.00
VI	56	-178	2.75	0.01
deoxyguanosine				
I	-103	52	0.00	0.63
II	63	59	0.37	0.34
III	-95	-56	2.51	0.01
IV	56	-63	2.91	0.00
V	-81	175	2.45	0.01
VI	63	-178	2.93	0.00

Table S2. Energies (E), wavelengths (λ), oscillator strengths (f) and dominant orbitals of the strongest transitions is some nucleic acid components, calculated at the B3LYP/6-311++G**/CPCM level.

Transition		E	E	λ	f	Principal orbitals relative to	
		eV	eV	nm		HOMO	→ LUMO
adenine[a]	1	4.88	4.99[c]	254	0.27	0	0
	3	5.16	5.23[c]	240	0.06	0	1
	7	5.89		210	0.24	-2	0
	11	6.36		195	0.23	-3	-3
cytosine[a]	1	4.74	4.87[b]	262	0.13	0	0
	3	5.38	5.48[b]	230	0.15	-1	-1
	7	5.99	6.05[b]	207	0.17	0	2
	12	6.50		191	0.61	-1	2
guanine[a]	1	4.73	4.87[c]	262	0.16	0	0
	2	5.00	5.24[c]	248	0.33	0	1
	5	5.53		224	0.01	0	3
	12	6.18		201	0.32	-2	0
	16	6.58		188	0.23	-2	1
thymine[a]	1	4.72	4.91[b]	263	0.24	0	0
	4	5.92	6.05[b]	209	0.23	0	2
	9	6.31	6.73[b]	203	0.00	-1	2
uracil[a]	1	4.94	5.09[b]	251	0.24	0	0
	5	6.04	6.09[b]	205	0.11	0	1
	6	6.16	6.25[b]	201	0.13	-2	0
guanine dimer	1	4.67		265	0.05	0	0
	5	4.92		252	0.10	0	2
	6	4.99		249	0.11	-1	2
	7	4.99		248	0.33	0	3
	30	6.16		201	0.19	-5	0
	31	6.18		201	0.23	-4	1
	47	6.54		189	0.13	-5	2
guanine-cytosine	1	4.14		300	0.01	0	0
	2	4.74		262	0.12	0	1
	3	4.88		254	0.16	-1	0
	5	5.05		246	0.36	0	2
	19	5.98		207	0.13	-1	2
	34	6.33		196	0.29	-4	1
	42	6.72		184	0.29	-2	4
G	1	4.75		261	0.15	0	0
	2	5.00		248	0.36	0	1
	11	6.03		205	0.27	-1	0
	15	6.29		197	0.15	-1	1

[a] all listed transitions are of A' symmetry.
[b] ref. [1], B3LYP/aug-cc-pVDZ/PCM.
[c] ref. [2], CC2/aug-cc-pVTZ/CPCM.

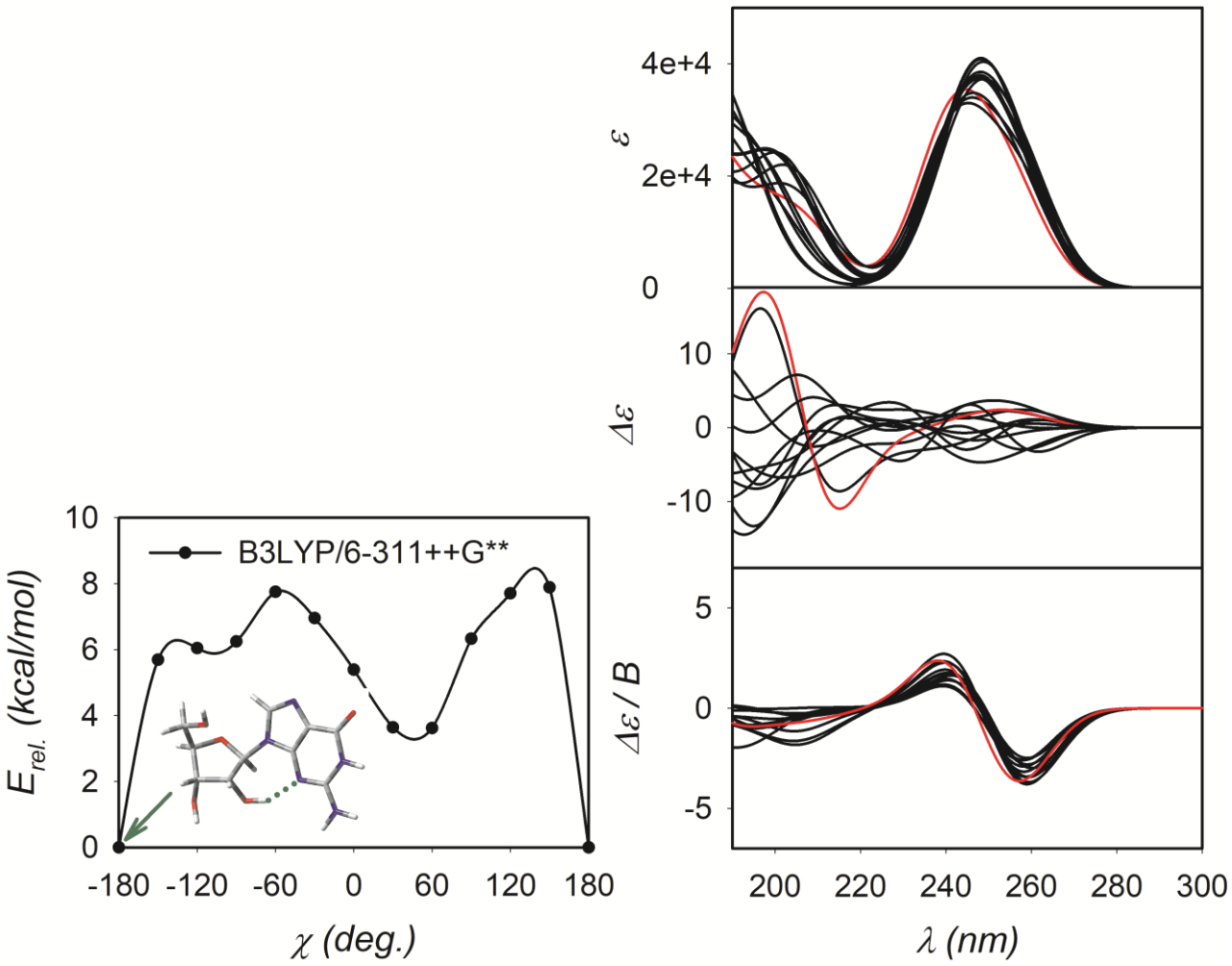


Figure S1. Dependence of the energy, absorption, ECD and MCD spectra on the χ torsion angle in guanosine, calculated at the B3LYP/6-31G**/CPCM level. In the minimum at χ ~ 180° an intramolecular H-bond is formed, spectra of this conformer are plotted in red.

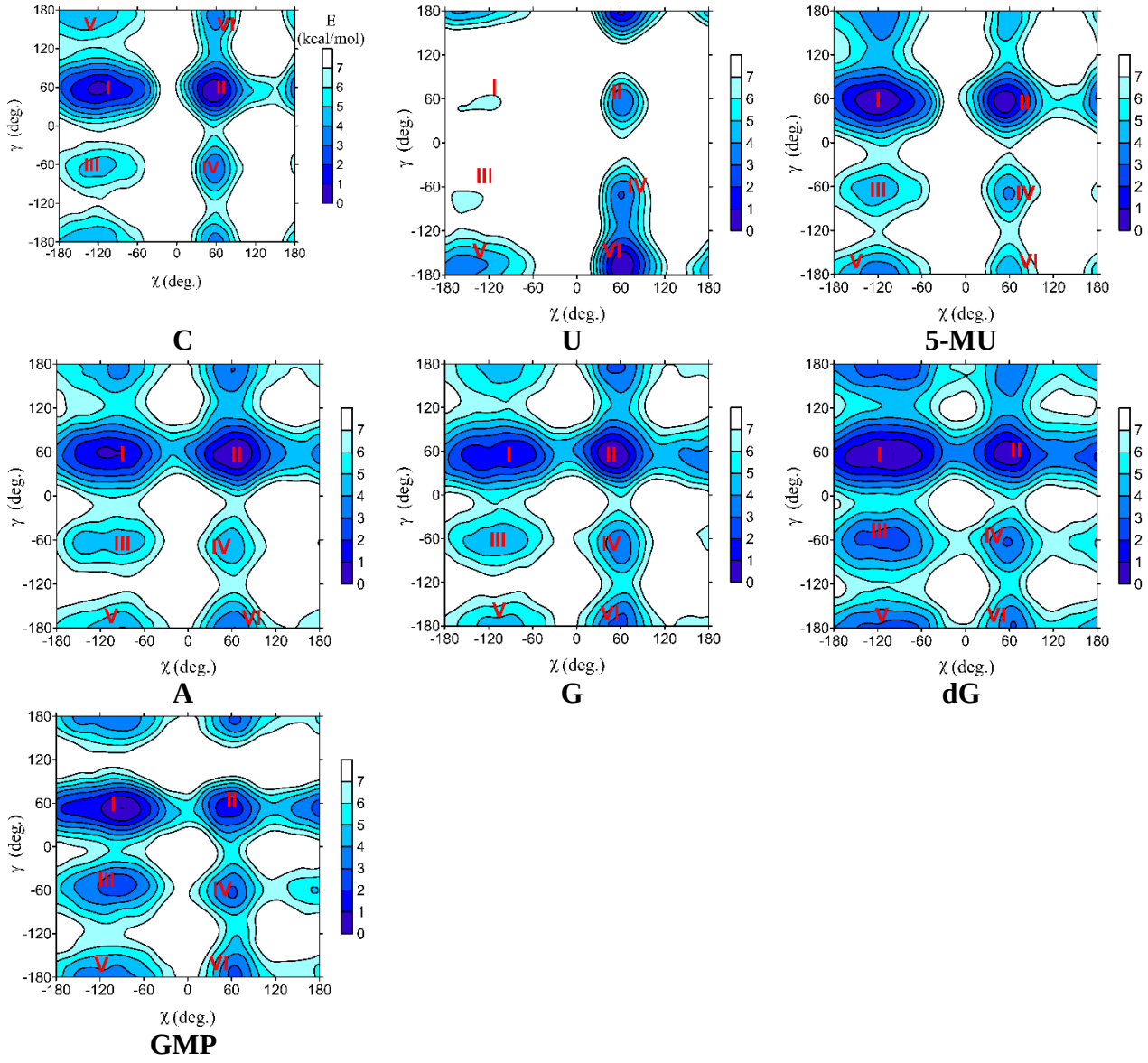


Figure S2. Dependence of free energy (kcal/mol) on the torsion angles (χ, γ **Figure 1**) for the studied nucleosides and GMP, as obtained from the metadynamics simulations.

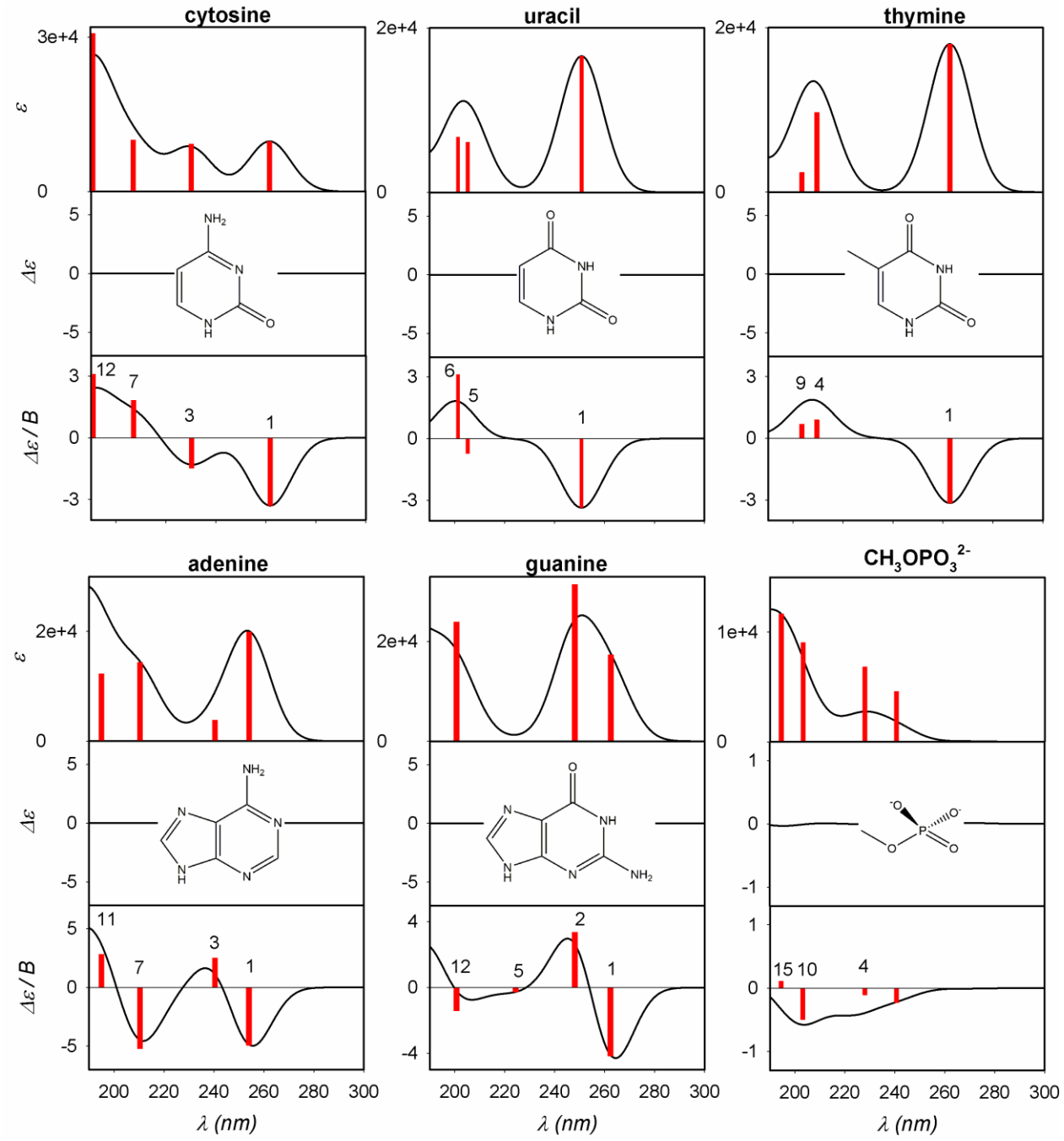
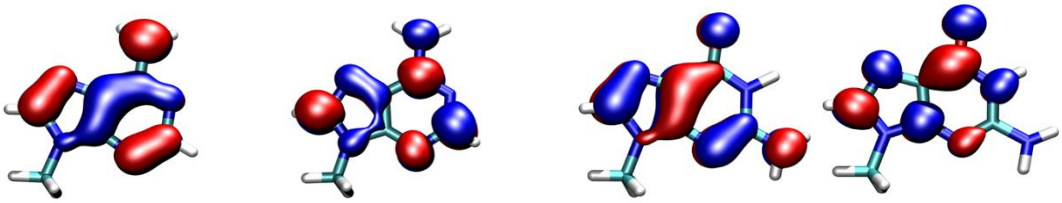


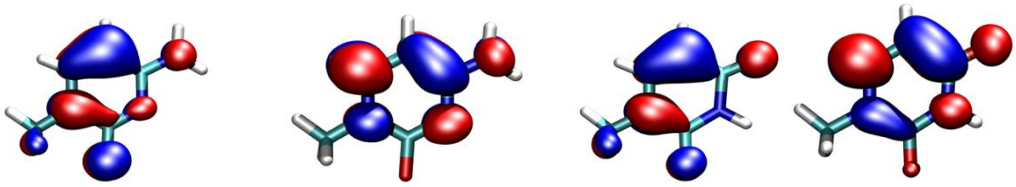
Figure S3. Calculated absorption (top) and MCD (bottom) spectra of five nucleobases and methylphosphate (B3LYP/6-311++G**/CPCM). The zero ECD lines (middle) were kept for consistency with other figures.

Adenine **Guanine**



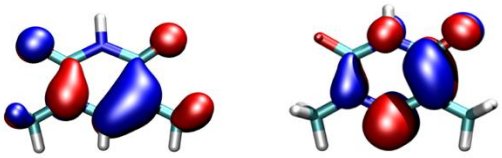
HOMO LUMO HOMO LUMO

Cytosine **Uracil**



HOMO LUMO HOMO LUMO

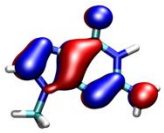
Thymine

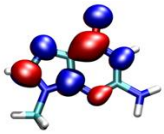


HOMO LUMO

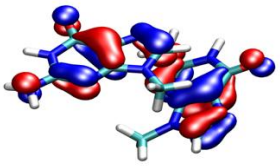
Figure S4. HOMO/LUMO orbitals in five nucleobases.

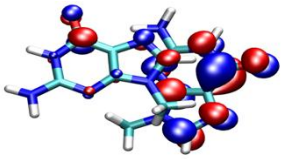
Guanine, plain

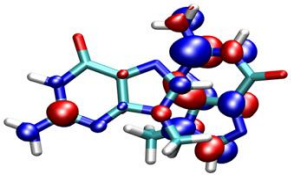

HOMO


LUMO

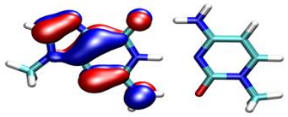
Guanine, stacked dimer

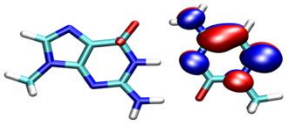

HOMO

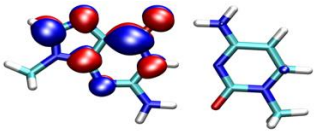

LUMO


LUMO+2

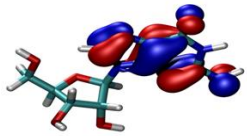
Guanine-cytosine planar dimer


HOMO


LUMO


LUMO+1

Guanosine


HOMO

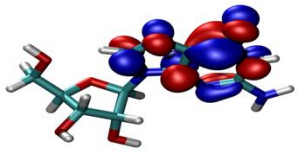

LUMO

Figure S5. Selected orbitals in four guanine-based nucleic acid components (B3LYP/6-311++G**/CPCM).

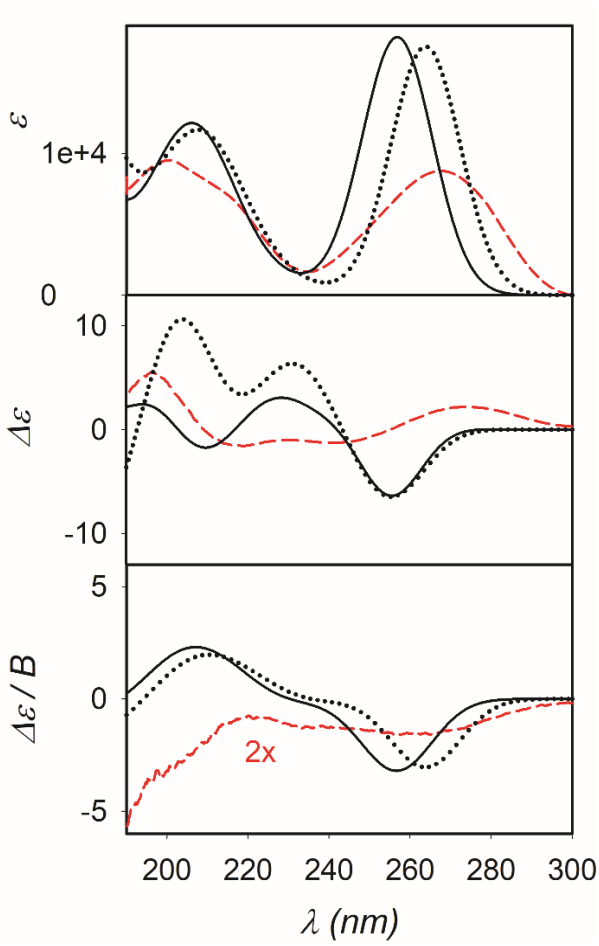


Figure S6. Calculated spectra of 5-MU with (dotted) and without (solid) explicit water molecules and the experiment (red dashed line). Calculations are for an average geometry over the six minima on the (χ, γ)-PES (B3LYP/6-311++G**/CPCM).

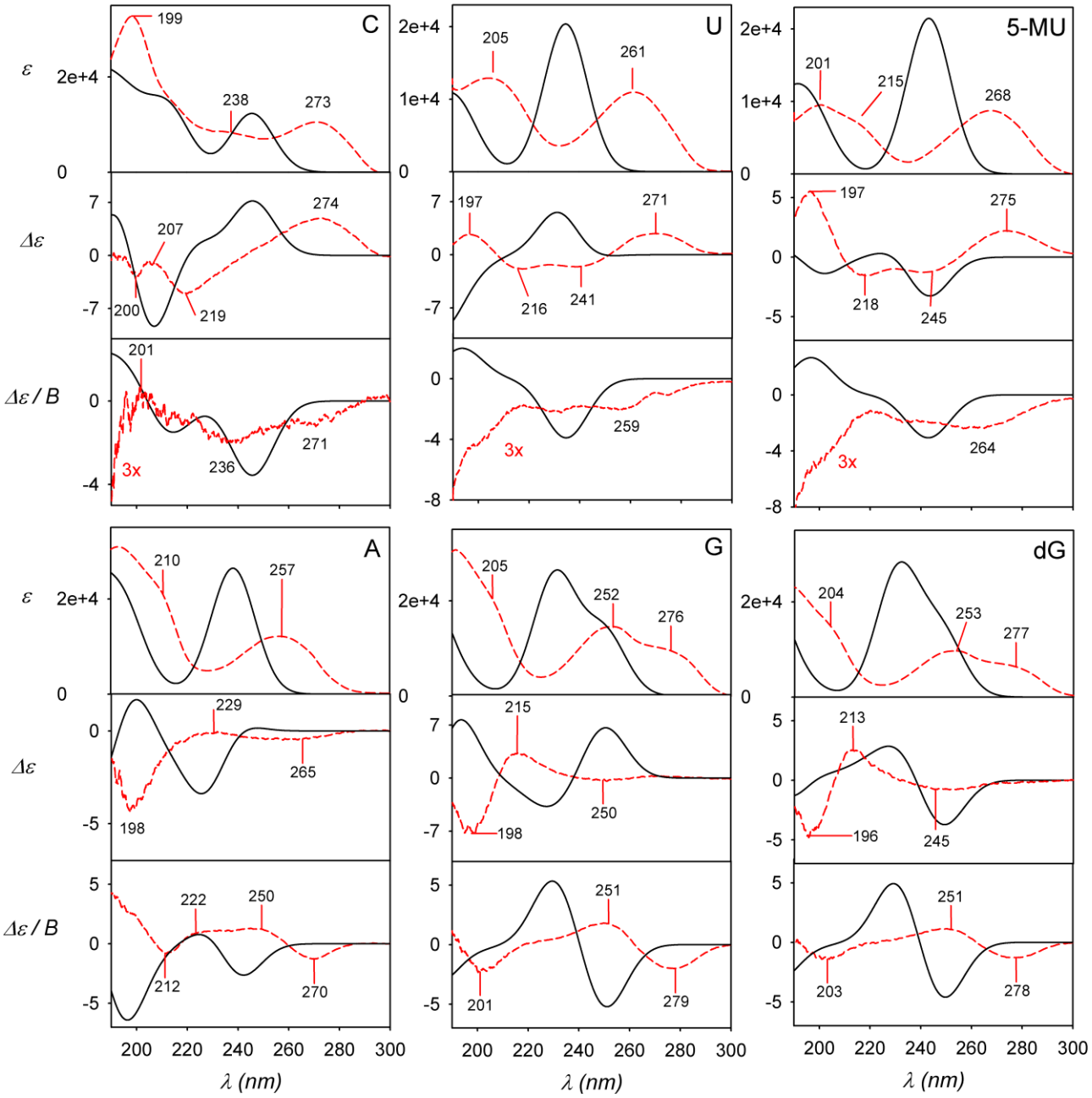


Figure S7. Calculated (black, solid) and experimental spectra of six nucleosides, a CAM-B3LYP/6-311++G**/CPCM weighted average over six geometries representing minima I-VI defined in **Figures 2** and **S2**.

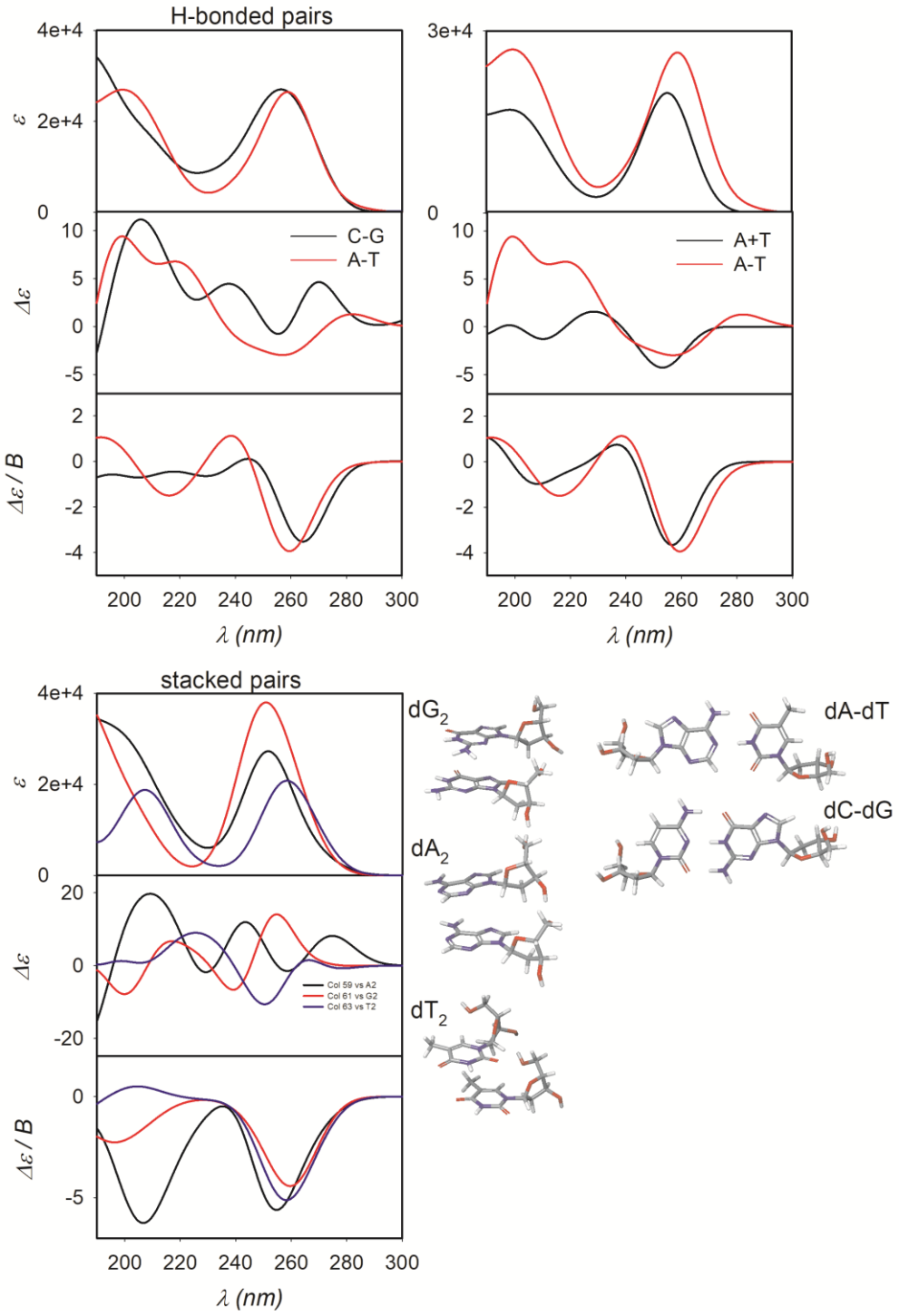


Figure S8. Simulated spectra of dC-dG and dA-dT as Watson-Crick H-bonded dimers (top left), dA-dT dimer and dA+dT plain sum (top right), and stacked $(dA)_2$, $(dG)_2$, $(dT)_2$ dimers in B-DNA geometry (bottom left).

References

1. T. Fahleson, J. Kauczor, P. Norman, F. Santoro, R. Improta and S. Coriani, *J. Phys. Chem. A*, 2015, **119**, 5476-5489.
2. S. K. Khani, R. Faber, F. Santoro, C. Hättig and S. Coriani, *J. Chem. Theory Comput.*, 2019, **15**, 1242-1254.