Theoretical Characterization of the reduction Potentials of nucleic acids in solution

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Supporting Information

1.1 Comparison of Vertical Ionization Energies (VIE) as obtained by different DFT functionals

VIEs of nucleobases have been obtained using different functionals: B3LYP, M06-2X and BP86.

Base	VIE (eV) B3LYP / 6-311++G(2d,2p)	VIE (eV) M06-2X / 6-311++G(2d,2p)	VIE (eV) BP86 / 6-311++G(2d,2p)
Adenine	8.21	8.48	8.85
Guanine	7.92	7.53	7.96
Cytosine	8.71	8.96	9.29
Thymine	8.97	9.23	9.58

1.2 Excitation Energies

The Excitation Energies have been evaluated using TDDFT (B3LYP/6-311++G(2d,2p)).

1.2.1 Excitation Energies for neutral nucleobases

Exc State	Adenine (eV)	Guanine (eV)	Cytosine (eV)	Thymine (eV)
1	4.92	4.54	4.58	4.69
2	4.94	4.81	4.74	4.91
3	5.15	4.98	5.09	5.40
4	5.20	5.13	5.17	5.76
5	5.41	5.24	5.39	5.91
6	5.55	5.52	5.55	6.09

1.2.2 Excitation Energies for radical-cation nucleobases in the equilibrium geometry of neutral nucleobases

Exc. State	Adenine (eV)	Guanine (eV)	Cytosine (eV)	Thymine (eV)
1	0.79	1.31	0.45	0.59
2	1.26	1.59	0.59	1.14
3	1.67	1.99	1.00	1.36
4	2.07	2.12	3.07	3.25
5	2.58	2.90	3.85	3.68
6	3.69	2.99	4.75	4.08

1.2.3 Excitation Energies for radical-cations nucleobases in the equilibrium geometry of the relaxed radical-cation nucleobase

Ex. en. State n.	Adenine (eV)	Guanine (eV)	Cytosine (eV)	Thymine (eV)
1	1.06	1.69	0.56	1.11
2	1.83	2.08	0.75	1.79
3	2.10	2.58	1.19	1.99
4	2.54	2.73	3.08	3.79
5	2.96	3.39	4.24	4.11
6	4.00	3.41	5.00	4.37

1.3 Standard reduction potentials of deoxynucleosides in water as obtained by PMM procedure and by different theoretical-computational methods reported in literature

Base	V_{red} (V) PMM *Deoxy nucleoside*	V_{red} (V) Psciuk et al.[1] *Nucleoside*	V_{red} (V) Li et al. *Nitrogenous base*	V_{red} (V) Paukku, Hill.[2] *Nitrogenous base*	V_{red} (V) Wang et al.[3] *Nitrogenous base*	V_{red} (V) Wang et al.[3] *Deoxy nucleoside*
Guanine	1.05	1.21	1.44	1.49	2.03	2.08
Adenine	1.26	1.52	1.71	1.86	2.38	2.44
Thymine	1.73	1.81	1.78	2.09	2.57	2.78
Cytosine	1.87	1.95	2.10	2.19	2.68	2.77

1.4 Standard reduction potentials of deoxynucleosides in acetonitrile solution as obtained by PMM procedure and by different theoretical-computational methods reported in literature

Base	V_{red} (V) PMM *Deoxy nucleoside*	V_{red} (V) Crespo-Hernandez et al.[4] *Nitrogenous base*	V_{red} (V) Crespo-Hernandez et al.[4] *syn-Deoxynucleoside*	V_{red} (V) Crespo-Hernandez et al.[4] *anti-Deoxyucleoside*
Guanine	1.18	2.04	2.04	1.82
Adenine	1.50	2.20	2.17	1.99
Thymine	1.64	2.62	2.41	2.24
Cytosine	1.79	2.44	2.34	2.12

The standard redox potentials are all reported against the reference standard hydrogen electrode ($V_{SHE} = 4.281\ V$).

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