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

Supporting Information

A fast but accurate excitonic simulation of the Electronic Circular Dichroism of Nucleic Acids: how can it be achieved?

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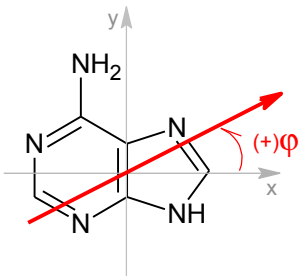
Table S1. RMSD analysis of the different structures of RNA β-hairpin (pdb code: 2KOC) and DNA G-quadruplex (pdb code: 143D). RMSD has been computed taking the first structure as a reference and considering only the heavy atoms of all the nucleobases included in the excitonic calculations (see Figure 1 and Figure 7 in the main text). Bold values are referred to the structures used in the calculations. The average RMSD values are also reported: ALL is computed by considering all the structures, SEL is computed by only including the bold structures.

Structure	**RMSD (Å)**	
	2KOC	**149D**
1	**0.000**	**0.000**
2	**0.624**	**0.719**
3	0.535	**0.765**
4	**0.557**	**0.855**
5	0.491	0.695
6	0.322	0.832
7	0.612	-
8	**0.357**	-
9	0.365	-
10	**0.497**	-
11	0.586	-
12	0.377	-
13	0.376	-
14	0.462	-
15	0.373	-
16	0.394	-
17	0.576	-
18	0.480	-
19	0.561	-
20	0.583	-
ALL-Average	0.480	0.773
SEL-Average	**0.509**	**0.800**

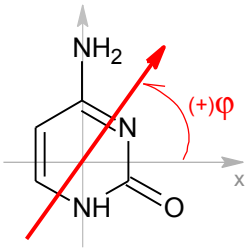
Table S2. First ten excited states of adenine computed at TD-M062X level of theory with two different basis sets. States in bold are referred to the π-π* bright transitions that have been used for the excitonic calculations. The angle φ of the transition dipole moment ***μ*** is defined in the figure at the head of the table.



	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-31G(d)	*1*	n-π*	5.39	230	0.000	0.13	0
	2	**π-π***	**5.58**	**222**	**0.248**	**3.43**	**-40**
	3	**π-π***	**5.67**	**219**	**0.057**	**1.62**	**-68**
	4	n-π*	5.95	209	0.001	0.25	0
	5	n-π*	6.42	193	0.002	0.29	0
	6	**π-π***	**6.89**	**180**	**0.431**	**4.06**	**-140**
	7	n-π*	6.97	178	0.017	0.80	0
	8	n-π*	7.20	172	0.000	0.06	0
	9	π-π*	7.24	171	0.021	0.87	-63
	10	π-π*	7.32	169	0.115	2.03	-65

	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-311+G(d)	*1*	n-π*	5.38	231	0.001	0.18	0
	2	**π-π***	**5.39**	**230**	**0.298**	**3.82**	**-44**
	3	**π-π***	**5.55**	**223**	**0.017**	**0.89**	**-116**
	4	π-R	5.68	218	0.006	0.54	0
	5	n-π*	5.91	210	0.002	0.27	**0**
	6	π-R	6.00	207	0.002	0.30	**0**
	7	n-π*	6.36	195	0.002	0.32	0
	8	π-R	6.51	191	0.002	0.28	0
	9	**π-π***	**6.63**	**187**	**0.276**	**3.31**	**-142**
	10	π-π*	6.67	186	0.188	2.73	-143

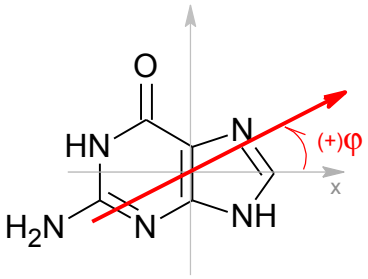
Table S3. First ten excited states of cytosine computed at TD-M062X level of theory with two different basis sets. States in bold are referred to the π-π* bright transitions that have been used for the excitonic calculations. The angle φ of the transition dipole moment ***μ*** is defined in the figure at the head of the table.



	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-31G(d)	***1***	**π-π***	**5.13**	**242**	**0.066**	**1.84**	**55**
	2	n-π*	5.29	234	0.001	0.24	0
	3	n-π*	5.85	212	0.000	0.12	0
	4	**π-π***	**6.14**	**202**	**0.152**	**2.55**	**-81**
	5	n-π*	6.47	192	0.000	0.08	0
	6	**π-π***	**7.02**	**177**	**0.436**	**4.05**	**-43**
	7	n-π*	7.05	176	0.001	0.21	0
	8	π-π*	7.37	168	0.205	2.71	-93
	9	π-R	7.57	164	0.000	0.09	0
	10	π-R	8.05	154	0.002	0.28	0

	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-311+G(d)	***1***	**π-π***	**5.02**	**247**	**0.074**	**1.97**	**53**
	2	n-π*	5.27	235	0.002	0.30	0
	3	π-R	5.68	218	0.003	0.38	0
	4	n-π*	5.85	212	0.000	0.10	0
	5	**π-π***	**5.96**	**208**	**0.142**	**2.51**	**-82**
	6	π-R	6.21	200	0.000	0.04	0
	7	π-R	6.34	196	0.011	0.66	0
	8	n-π*	6.43	193	0.000	0.06	0
	9	π-R	6.59	188	0.004	0.40	0
	10	**π-π***	**6.59**	**188**	**0.413**	**4.06**	**-39**

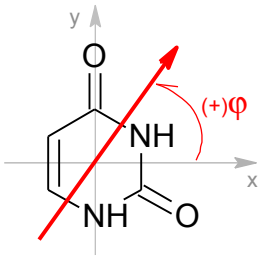
Table S4. First ten excited states of guanine computed at TD-M062X level of theory with two different basis sets. States in bold are referred to the π-π* bright transitions that have been used for the excitonic calculations. The angle φ of the transition dipole moment ***μ*** is defined in the figure at the head of the table.



	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-31G(d)	***1***	**π-π***	**5.34**	**232**	**0.172**	**2.92**	**45**
	2	n-π*	5.45	227	0.000	0.13	0
	3	**π-π***	**5.89**	**211**	**0.316**	**3.76**	**-23**
	4	n-π*	6.45	192	0.005	0.43	0
	5	n-π*	6.63	187	0.001	0.16	0
	6	π-R	7.04	176	0.000	0.11	0
	7	π-π*	7.05	176	0.009	0.57	-75
	8	n-π*	7.50	165	0.004	0.36	0
	9	π-π*	7.55	164	0.345	3.47	-4
	10	n-π*	7.60	163	0.005	0.41	0

	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-311+G(d)	*1*	π-R	5.02	247	0.002	0.34	0
	2	**π-π***	**5.18**	**239**	**0.176**	**2.99**	**51**
	3	π-R	5.45	228	0.002	0.30	0
	4	π-R	5.47	227	0.002	0.28	0
	5	**π-π***	**5.63**	**220**	**0.342**	**4.01**	**-21**
	6	π-R	6.06	205	0.001	0.16	0
	7	π-R	6.12	203	0.001	0.22	0
	8	n-π*	6.34	195	0.003	0.37	0
	9	π-R	6.37	195	0.014	0.77	-37
	10	π-R	6.50	191	0.000	0.05	0

Table S5. First ten excited states of uracile computed at TD-M062X level of theory with two different basis sets. States in bold are referred to the π-π* bright transitions that have been used for the excitonic calculations. The angle φ of the transition dipole moment ***μ*** is defined in the figure at the head of the table.



	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-31G(d)	*1*	n-π*	4.97	249	0.000	0.07	0
	2	**π-π***	**5.66**	**219**	**0.187**	**2.95**	**-81**
	3	n-π*	6.26	198	0.000	0.02	0
	4	**π-π***	**6.81**	**182**	**0.040**	**1.25**	**-64**
	5	**π-π***	**7.20**	**172**	**0.157**	**2.40**	**13**
	6	n-π*	7.51	165	0.000	0.07	0
	7	n-π*	7.66	162	0.000	0.01	0
	8	π-R	7.74	160	0.000	0.05	0
	9	π-π*	8.01	155	0.383	3.55	-62
	10	π-R	9.30	133	0.004	0.33	0

	Transition		E (eV)	λ (nm)	*f*	μ (D)	φ (deg)
M062X/6-311+G(d)	*1*	n-π*	4.99	248	0.000	0.02	0
	2	**π-π***	**5.51**	**225**	**0.202**	**3.11**	**-81**
	3	π-R	6.05	205	0.003	0.33	0
	4	n-π*	6.26	198	0.000	0.02	0
	5	**π-π***	**6.69**	**185**	**0.040**	**1.25**	**-83**
	6	**π-π***	**6.88**	**180**	**0.185**	**2.66**	**6**
	7	π-R	7.00	177	0.001	0.22	0
	8	π-R	7.06	176	0.016	0.77	0
	9	n-π*	7.46	166	0.002	0.25	0
	10	π-R	7.51	165	0.011	0.63	-81

Table S6. Mean Absolute Difference (MAD) of π-π* transition energies between DFT and experimental values. MAD is defined as $\langle|E - \bar{E}|\rangle$, where $\bar{E}$ is the reference excitation energy (that corresponds to the experimental value in this case). All values are in eV.

	6-31G(d)	**6-311+G(d)**
Adenine	0.91	0.73
Cytosine	0.67	0.42
Guanine	0.91	0.70
Uracile	0.62	0.43

Table S7. Coefficient matrix of 1-RNA structure computed at TD-M062X/6-31G(d) level using the SS model for site energies. The coefficients corresponds to the $\left|c_{mi}^{(k)}\right|^2$ (see Eq.1). Each row refers to an excitonic states *k*; columns are referred to the local transition *i* on chromophore *m*. Excitation energy (E), square modulus of the electric transition dipole moment (μ^2), rotational strength (R) and delocalization length (L) are also reported in the first four column of the table for each excitonic state.

#	E	μ^2	R	L	G1		G2		C3			A4			C5			U6			G9		G10		U11		G12		C13			C14		
	(eV)	*(D^2)*	*(10^{-40} cgs)*		G(1)	G(2)	G(1)	G(2)	C(1)	C(2)	C(3)	A(1)	A(2)	A(3)	C(1)	C(2)	C(3)	U(1)	U(2)	U(3)	G(1)	G(2)	G(1)	G(2)	U(1)	U(2)	U(3)	G(1)	G(2)	C(1)	C(2)	C(3)	C(1)	C(2)	C(3)
1)	4.404	0.24	37	2.2	0.41	0	0.53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.06	0	0	0	0	0	0
2)	4.421	0.24	60	1.9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.34	0	0.65	0	0.01	0	0	0	0	0	0	0	0	0
3)	4.434	0.15	-38	1.3	0.12	0	0	0	0	0	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.86	0	0.01	0	0	0	0
4)	4.463	1.57	46	1.9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.66	0	0.32	0	0.01	0	0	0	0	0	0	0	0	0
5)	4.477	1.99	-131	2.4	0.46	0	0.46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.06	0	0	0	0	0	0
6)	4.592	0.4	32	2.3	0	0	0	0	0.06	0	0	0.57	0.01	0	0.33	0	0	0	0	0	0	0	0	0	0.02	0	0	0.01	0	0	0	0	0	0
7)	4.627	0.08	27	2.1	0	0	0	0	0.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.51	0	0	0.46	0	0
8)	4.637	0.3	90	1.6	0	0	0	0	0.78	0	0	0	0	0	0.16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.04	0	0
9)	4.65	0.67	-174	2.3	0	0	0	0	0	0	0	0.01	0	0	0.04	0	0	0	0	0	0	0	0	0	0	0	0	0	0.44	0	0	0	0.48	0	0
10)	4.664	2.56	79	3.0	0	0	0	0	0.12	0	0	0.36	0.01	0	0.43	0	0	0	0	0	0	0	0	0.01	0.02	0	0	0	0.03	0	0	0	0.01	0	0
11)	4.756	0.22	3	1.7	0	0	0	0	0	0	0	0.01	0.73	0	0.01	0	0	0	0	0	0	0	0	0	0.24	0	0	0	0	0	0	0	0	0	0
12)	4.792	1.14	190	1.2	0	0	0	0	0	0	0	0	0.03	0	0	0	0	0.91	0	0	0	0.01	0	0	0.04	0	0	0	0	0	0	0	0	0	0
13)	4.814	1.46	-302	2.6	0	0	0	0	0	0	0	0.02	0.2	0	0.01	0	0	0.06	0	0	0	0	0.02	0.02	0.58	0	0	0	0.07	0	0	0	0	0	0
14)	4.902	0.72	327	2.2	0	0.45	0	0.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.03	0	0	0	0	0	0
15)	4.944	0.71	-118	2.7	0	0.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.31	0	0.5	0	0	0	0.16	0	0	0	0	0	0
16)	4.952	2.45	1382	2.4	0	0.04	0	0	0	0	0	0	0	0	0	0	0	0.01	0	0	0	0.57	0	0.06	0.01	0	0	0.3	0	0	0	0	0	0	0
17)	4.967	4.79	-1922	3.6	0	0.08	0	0.02	0	0	0	0	0.01	0	0	0	0	0	0	0	0	0.11	0	0.4	0.06	0	0	0.3	0	0	0	0	0	0	0
18)	5.002	1.97	407	2.7	0	0.39	0	0.45	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0.01	0	0	0.11	0	0	0	0	0	0	0
19)	5.369	0.17	-13	2.4	0	0	0	0	0	0.19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.56	0	0	0	0.24	0	0
20)	5.394	0.14	-115	3.0	0	0	0	0	0	0.36	0	0	0	0	0	0.24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0	0	0.39	0	0
21)	5.399	0.8	297	1.8	0	0	0	0	0	0.1	0	0	0	0.01	0	0.73	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0	0	0.14	0	0
22)	5.452	2.99	-228	3.0	0	0	0.01	0.01	0	0.33	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.42	0	0	0.22	0	0
23)	5.949	0.91	38	1.5	0	0	0	0	0	0	0	0	0	0.81	0	0.01	0.09	0	0	0	0	0	0	0	0.09	0	0	0	0	0	0	0	0	0	0	0
24)	6.097	0.11	-22	1.2	0	0	0	0	0	0	0	0	0	0	0	0	0.02	0	0.92	0	0	0	0	0	0.05	0	0	0	0	0	0	0	0	0	0	0
25)	6.112	0.22	75	1.4	0	0	0	0	0	0	0	0	0	0.06	0	0	0.04	0	0.06	0	0	0	0	0	0.84	0	0	0	0	0	0	0	0	0	0	0
26)	6.253	0.22	76	2.5	0	0	0	0	0	0	0.38	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.04	9	0	0	0	0.12
27)	6.3	1.77	822	1.6	0	0	0	0	0	0	0.24	0	0	0	0	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.74
28)	6.363	6.14	49	1.4	0	0	0	0	0	0	0.01	0	0	0.12	0	0	0.82	0	0.01	0	0	0	0	0	0.02	0	0	0	0	0	0	0	0	0	0	0.01
29)	6.37	6.39	-1003	2.5	0	0	0	0	0	0	0.36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.05	0	0	0	0	0.13
30)	6.898	0.12	199	2.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.53	0	0	0	0	0	0.47	0	0	0	0	0	0	0	0	0	0	0
31)	6.907	1.88	-184	2.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.47	0	0	0	0	0	0.53	0	0	0	0	0	0	0	0	0	0	0

Table S8. Coefficient matrix of 1-GQ structure computed at TDM062X/6-31G(d) level. The coefficients corresponds to the $\left|c_{mi}^{(k)}\right|^2$ (see Eq.1). Each row refers to an excitonic states *k*; columns are referred to the local transition *i* on chromophore *m*. Excitation energy (E), square modulus of the electric transition dipole moment (μ^2), rotational strength (R) and delocalization length (L) are also reported in the first four column of the table for each excitonic state.

#	E	μ^2	R	L	G2		G3		G4		G8		G9		G10		G14		G15		G16		G20		G21		G22	
	(eV)	*(D^2)*	*(10^{-40} cgs)*		G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)	G(1)	G(2)
1)	5.264	0.20	488	8.05	0.01	0	0.14	0	0.14	0	0.13	0	0.17	0	0	0	0.02	0	0.09	0	0.05	0	0.09	0	0.14	0	0.02	0
2)	5.292	0.10	27	4.88	0.25	0	0.1	0	0.01	0	0	0	0	0	0.09	0	0.01	0	0.22	0	0.27	0	0	0	0.02	0	0.02	0
3)	5.295	0.10	-95	5.24	0.11	0	0	0	0.01	0	0.01	0	0.02	0	0.06	0	0.32	0	0.23	0	0.07	0	0.04	0	0	0	0.11	0
4)	5.317	0.00	86	6.73	0.09	0	0.18	0	0.01	0	0.09	0	0.06	0	0.17	0	0	0	0.05	0	0	0	0.04	0	0.05	0	0.25	0
5)	5.321	0.20	274	7.08	0.04	0	0.09	0	0	0	0.01	0	0.13	0	0.21	0	0.08	0	0.01	0	0.21	0	0.14	0	0.02	0	0.04	0
6)	5.331	0.40	-70	6.67	0.08	0	0.05	0	0.01	0	0.04	0	0.13	0	0.13	0	0.03	0	0	0	0.02	0	0.26	0	0.18	0	0.07	0
7)	5.341	0.90	63	3.25	0	0	0.07	0	0.51	0	0.07	0	0.06	0	0	0	0	0	0	0	0	0	0.02	0	0.14	0	0.1	0
8)	5.349	1.50	-351	2.91	0	0	0.01	0	0.16	0	0.54	0	0.01	0.01	0.04	0	0	0	0.01	0	0.03	0	0.02	0	0.17	0	0	0
9)	5.358	1.60	74	5.22	0.02	0	0.05	0	0.02	0	0.02	0	0.11	0	0.02	0	0.33	0	0	0	0.02	0	0.17	0	0.04	0	0.19	0
10)	5.364	5.30	-61	7.22	0.22	0	0.17	0	0.03	0	0.02	0	0.02	0	0.04	0	0.09	0	0.01	0	0.01	0	0.14	0	0.15	0	0.1	0
11)	5.379	1.20	-138	6.21	0.12	0	0.05	0	0.06	0	0.06	0	0.28	0	0.23	0	0	0	0.03	0	0.06	0	0.02	0	0.01	0	0.07	0
12)	5.412	1.70	-130	5.11	0.04	0	0.09	0.01	0.03	0	0	0	0.01	0	0	0	0.1	0	0.33	0	0.24	0	0.05	0	0.06	0	0.02	0
13)	5.789	0.20	76	2.97	0	0	0	0	0	0	0	0.02	0	0.04	0	0	0	0.23	0	0	0	0	0	0.22	0	0.48	0	0
14)	5.804	0.50	-155	3.42	0	0.03	0	0.02	0	0.01	0	0.29	0	0.44	0	0.06	0	0	0	0	0	0	0	0.01	0	0.03	0	0.11
15)	5.811	0.30	-52	2.76	0	0.14	0	0.01	0	0.01	0	0.01	0	0.01	0	0	0	0.02	0	0.51	0	0.29	0	0	0	0	0	0
16)	5.821	0.30	-165	3.22	0	0.06	0	0.42	0	0.36	0	0.04	0	0.01	0	0.04	0	0.01	0	0.01	0	0.02	0	0.02	0	0	0	0.01
17)	5.869	2.00	-836	3.05	0	0.06	0	0	0	0.01	0	0.22	0	0	0	0.07	0	0.02	0	0	0	0.01	0	0.09	0	0	0	0.51
18)	5.871	1.60	-862	3.67	0	0.01	0	0.01	0	0.08	0	0.03	0	0.01	0	0.4	0	0.25	0	0	0	0	0	0.2	0	0	0	0
19)	5.881	0.60	-346	4.53	0	0.19	0.01	0	0	0.2	0	0	0	0	0	0.03	0	0.08	0	0.01	0	0.35	0	0.1	0	0	0	0.01
20)	5.918	0.50	152	5.97	0	0.15	0	0	0	0.01	0	0.04	0	0	0	0.27	0	0.12	0	0.01	0	0.1	0	0.09	0	0	0	0.2
21)	5.941	8.20	862	4.51	0.01	0.24	0	0.37	0	0.11	0	0.02	0	0	0	0.05	0	0	0	0.12	0	0.06	0	0.01	0	0.02	0	0
22)	5.953	11.00	854	8.76	0	0.04	0	0.07	0	0.12	0	0.1	0	0.15	0	0.05	0	0.05	0	0.21	0	0.09	0	0.05	0	0.05	0	0.02
23)	5.965	3.80	239	6.06	0	0.02	0	0	0	0	0	0.14	0	0.21	0	0.01	0	0.13	0	0.03	0	0	0	0.09	0	0.26	0	0.1
24)	6.108	0.20	72	10.82	0	0.04	0	0.08	0	0.08	0	0.09	0	0.12	0	0.02	0	0.08	0	0.1	0	0.08	0	0.1	0	0.15	0	0.04

Figure S1. Comparison between the M062X/6-311+G(d) CD spectra of 1-RNA structure using the simplified (μμ, black) and the full (μμ+μm, red) formulation of the rotational strength.

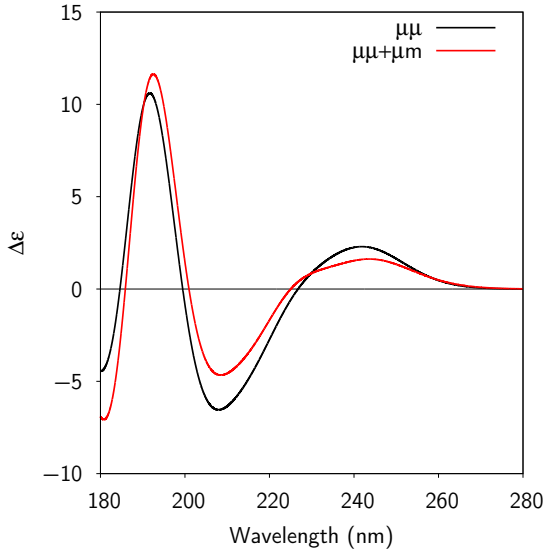


Figure S2. Comparison between the M062X/6-31G(d) CD spectra (SS model) of 1-RNA structure by including the first 5 base pair (red curve) or also the sixth pair, U6-G9 (black curve).

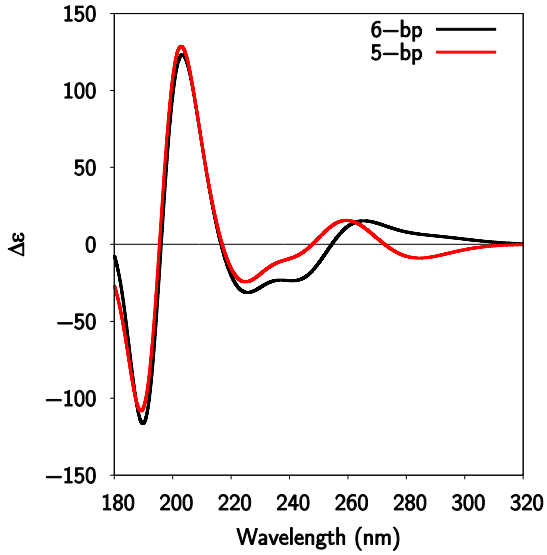


Figure S3. Comparison between CD spectra of the 1-RNA structure computed at M062X/6-31G(d) by using the SS model for the site energies (black curve). The SS* model (red curve) is obtained by inverting the site energies assignment of the first two π- π* states of adenine.

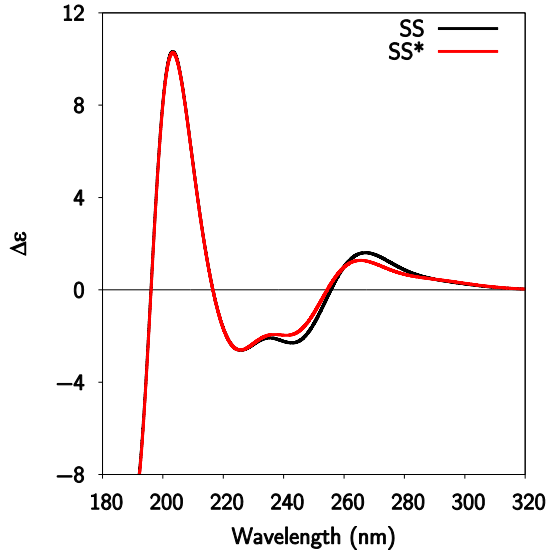


Figure S4. Absorption (top) and CD (bottom) spectra of 1-RNA structure simulated at M062X/6-31G(d) (SS model) by using the PDA for couplings. Black curves represent the total spectra. Colored curves represent the contributions from specific groups of excitonic states identified by different colors. Vertical bars correspond to square dipole moments and rotational strengths.

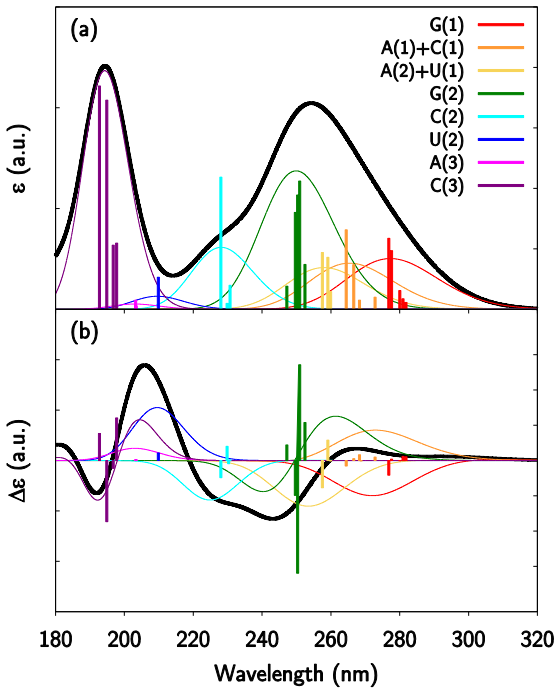


Figure S5. Comparison between CD spectra of the 1-GQ structure computed at TD-M062X/6-311+G(d) including up to 10 transitions of each nucleobase (black curve), and only the first π- π* transitions (red curve). Green curve corresponds to TD-M062X/6-31G(d) including only the first π- π* transitions.