Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Sequence dependence on DNA photochemistry: a computational study of photodimerization pathways in TpdC and dCpT dinucleotides.

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Supporting Information. **Pages**

1. Computational Details

The ground state minima of TpC and CpT conformers were optimized using the Density Functional Theory (DFT) and their vertical absorption energies (VAEs) and excited state Potential Energy Surfaces characterized by means on its Time Dependent (TD-DFT) extension. We have selected the M052X[1, 2] functional due to its good performance for treating stacked systems. For geometry optimizations and VAEs the M052X functional was combined with the 6-31G(d) basis set. However, larger basis sets (6-31+G(d,p) and 6-311+G(2d,2p)) were considered for computing the relative stability of the different conformers.

Polarizable Continuum Model (PCM)[3, 4] was used to account for bulk solvent effects, describing the excited states with Linear Response PCM/TD-DFT implementation,[5] for which analytic gradient are available.[6] For some specific cases (i.e. Charge Transfer states), State Specific-PCM[7] single points were performed since it provides a more accurate description of the electronic transitions involving a large density shift.

All the calculations have been performed using the Gaussian 09 program.[8]

2. Results

2.1. Conformational Study

Figure S1. Comparison between the ground state optimized minima (PCM/M052X/6-31G(d)) of the TpC in the different conformations. Geometries have been aligned respect to the thymine base. a) d22 is the distance between the middle points of C5-C6 thymine and cytosine bonds; b) d64 is the distance between C6 in thymine and C4 in cytosine.

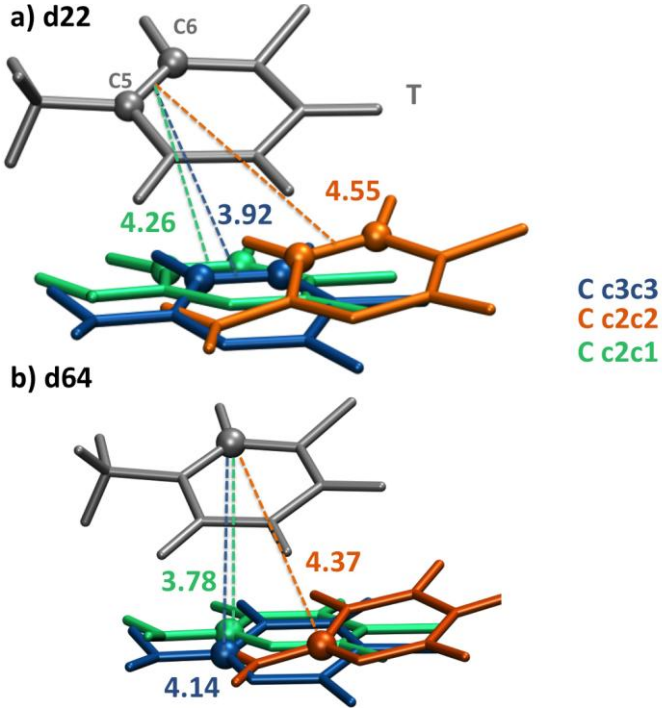


Table S1. Relative energies (in kcal/mol) for the different conformers of TpC and CpT with the specified level of theory.

	TpC			CpT		
	c3c3	c2c2	c2c1	c3c3	c2c2	c2c1
PCM/M052X/ 6-31G(d)	0.00	0.47	0.45	0.00	3.40	3.42
PCM/M052X/ 6-31+G(d,p)	0.00	0.45	0.35	0.00	3.07	2.54
PCM/M052X/ 6-311+G(2d,2p)	0.00	0.31	0.09	0.00	3.19	2.43

2.2. Excited State at the FC region

Table S2. Main transition character, coefficients (coeff.), energies (E, in eV) and oscillator strength (f, in parenthesis) for the lowest energy excited states computed at the PCM/TD-M052X/6-31G(d) levels of theory in TpC and CpT conformers. [a]The molecular orbital are very mixed so in this stable we just adopt the following nomenclature: HOMO-1=T, HOMO=C, LUMO=T and LUMO+1=C.

TpC	**[a]c3c3**		**[a]c2c2**		**[a]c2c1**	
	Coeff.	ΔE (f)	Coeff.	ΔE (f)	Coeff.	ΔE (f)
□□	T->C 0.35 C->T 0.48 C->C -0.45	5.16 (0.041)	T->T 0.29 T->C -0.31 C->T 0.48 C->C -0.23	5.13 (0.095)	T->T 0.35 C->T 0.22 C->C 0.50	5.21 (0.037)
□2	**nπ***	5.20 (0.001)	**nπ***	5.19 (0.001)	**nπ*+ ππ***	5.22 (0.014)
□3	T->T 0.53 C->C 0.36	5.35 (0.379)	T->T -0.33 C->C 0.47	5.33 (0.342)	T->T -0.44 C->C -0.29	5.33 (0.358)
□4	**nπ***	5.71 (0.004)	**nπ***	5.69 (0.003)	**nπ***	5.66 (0.006)
□5	T->T -0.38 T->C -0.19 C->T 0.40 C->C 0.33	6.01 (0.007)	**nπ***	6.12 (0.063)	**nπ***	6.04 (0.012)
□6	**nπ***	6.11 (0.002)	T->T 0.31 T->C -0.31 C->T -0.30 C->C 0.26	6.13 (0.083)	T->T 0.35 T->C 0.47 C->T 0.16 C->C 0.25	6.10 (0.027)
□8	T->C 0.47	6.19 (0.044)	T->T 0.31 T->C 0.45 C->T 0.25 C->C 0.32	6.34 (0.019)	T->T -0.18 T->C 0.13 C->T 0.55 C->C -0.35	6.28 (0.014)
CpT	**[a]c3c3**		**[a]c2c2**		**[a]c2c1**	
□□	T->T 0.22 T->C -0.35 C->T 0.54 C->C -0.11	5.12 (0.126)	T->T 0.16 T->C 0.41 C->T 0.27 C->C 0.45	5.19 (0.163)	C->T -0.32 C->C 0.59	5.09 (0.138)
□2	**nπ***	5.22 (0.007)	**nπ***	5.20 (0.001)	**nπ***	5.17 (0.002)
□3	T->T 0.48 C->T -0.29 C->C -0.37	5.27 (0.226)	T->T 0.45 T->C -0.17 C->T -0.42 C->C 0.24	5.36 (0.266)	T->T 0.63	5.37 (0.231)
□4	**nπ***	5.73 (0.003)	**nπ***	5.74 (0.002)	**nπ*+ ππ***	5.64 (0.014)
□5	T->T 0.42 C->C 0.55	5.97 (0.006)	**nπ***	6.07 (0.007)	C->T 0.61	5.81 (0.018)
□6	T->C 0.58 C->T 0.32 T->T 0.14	6.02 (0.033)	T->T 0.41 T->C -0.22 C->T 0.40 C->C -0.21	6.14 (0.011)	**nπ***	6.07 (0.009)
□8	C->T 0.55 C->C -0.33 T-C 0.12	6.18 (0.170)	T->T 0.22 T->C 0.47 C->T 0.18 C->C 0.38	6.44 (0.023)	T->C 0.56	6.22 (0.093)

Figure S2. Excited state density difference (S_0-S_n, negative red, positive green, grid=0.003) of the indicated excited states (S_n) for the different conformers of TpC dinucleotide.

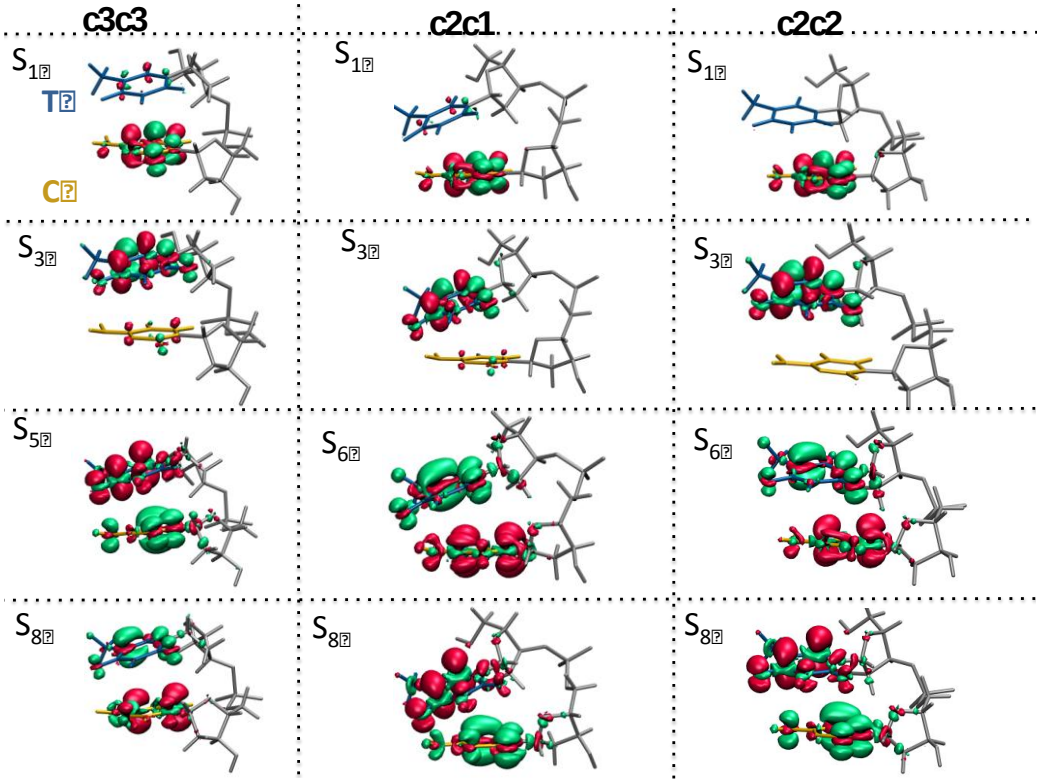
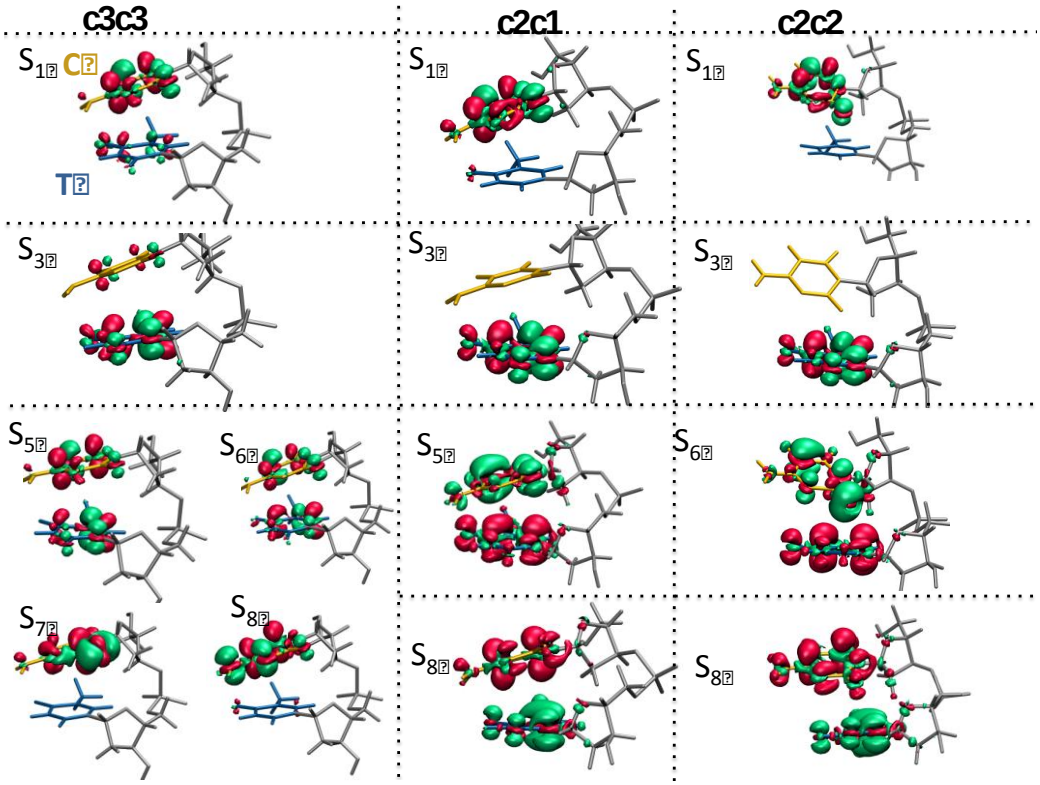


Figure S3. Excited state density difference (S_0-S_n, negative red, positive green, grid=0.003) of the indicated excited states (S_n) for the different conformers of CpT dinucleotide.



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