SUPPORTING INFORMATION

Directional and Regioselective Hole injection in A/T-rich DNA Induced by Intercalated Spiropyran Photoswitches

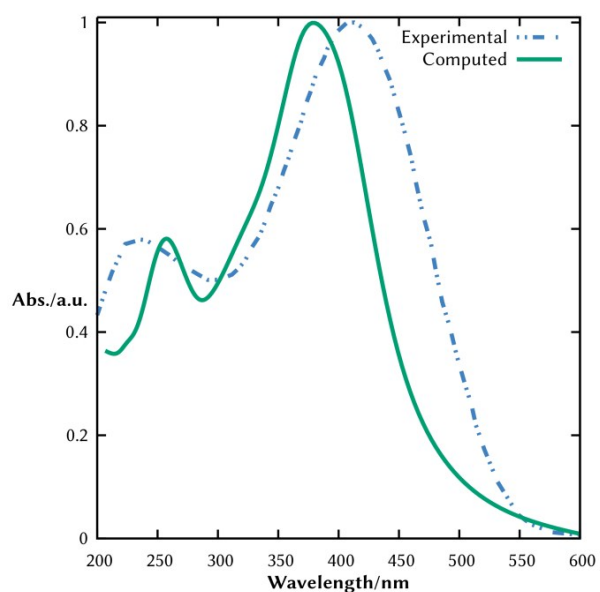Davide Avagliano, Pedro A. Sánchez-Murcia* and Leticia González*

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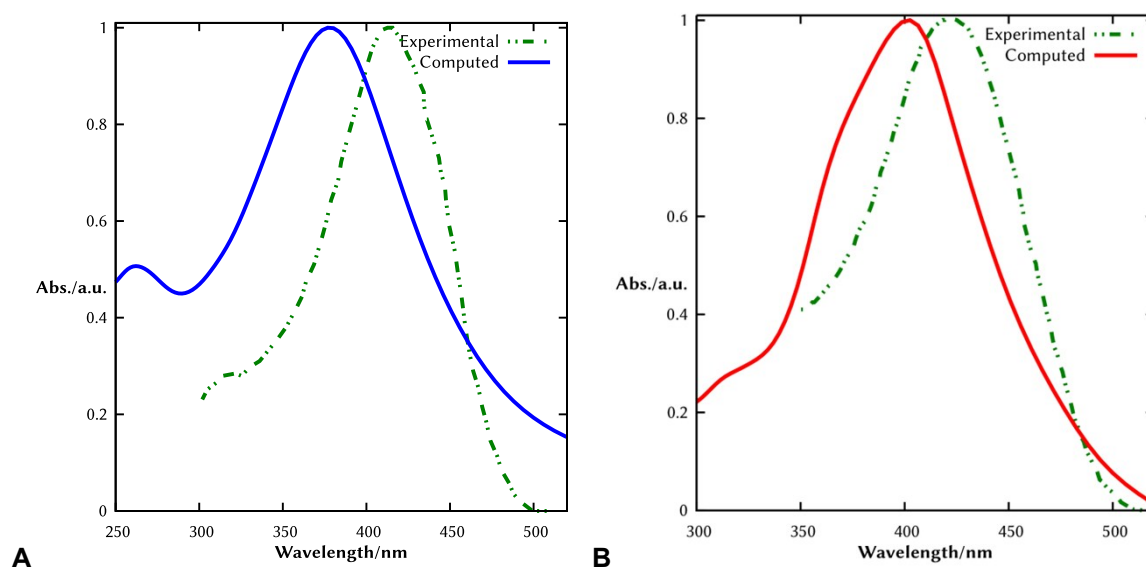* leticia.gonzalez@univie.ac.at

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Figure S1. Comparison between computed and experimental spectra of **2a** in water.[1]


Figure S2 Comparison between computed and experimental spectra of **2b** in water[2] (**A**) and DNA environment[2] (**B**). We reproduced the lower energy absorption band in the limit of error of our method and the small red shift induced by DNA embedding.

Table S1. Energy (eV), oscillator strength (*f*), CT number and excited electron/hole population (in parenthesis the fragment of e/h localization) for the first five excited singlet states of the minimum energy geometry of **2b**:DNA.

State	Energy	*f*	CT number	electron hole	excited electron
S_1	2.79	0.012	0.980	0.956 (**t-A**)	0.897 (**2a**)
S_2	3.20	0.002	0.997	0.956 (**t-A**)	0.896 (**c-T**)
S_3	3.24	0.907	0.057	0.877 (**2b**)	0.980 (**2b**)
S_4	3.67	0.009	0.991	0.943 (**t-T**)	0.924 (**2a**)
S_5	3.71	0.004	0.982	0.935 (**t-A**)	0.868 (**2a**)

Table S2. Average distances (Å) between the center of mass (COM) of probes **2a** and **2b** and the COM of the four surrounding nucleobases on the coding (c-T,c-A) and on the template strand (t-T, t-A) along the QM/MM MD simulations. Distances computed with the *cpptraj* program of AMBER suite.

	distance between COMs (Å)			
	c-A	*c-T*	*t-A*	*t-T*
2a:DNA	4.12	5.16	4.13	4.97
2b:DNA	4.31	5.83	4.24	5.09
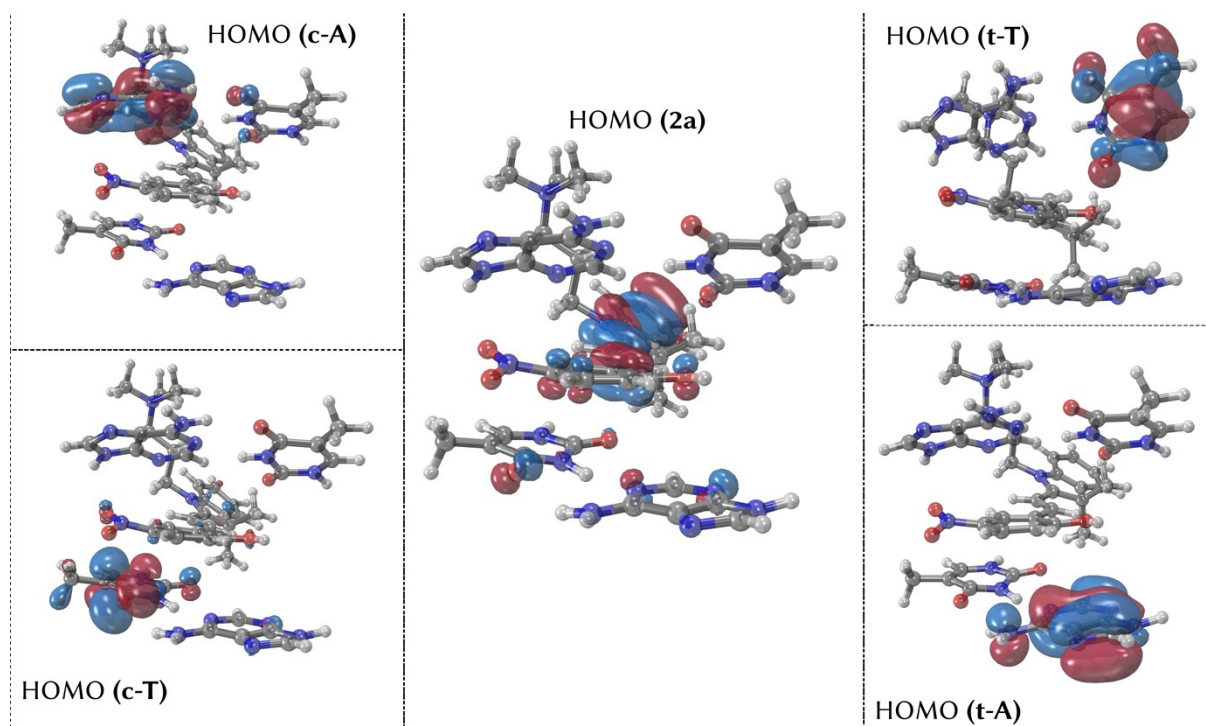
Figure S3. HOMO of the photoprobe **2a** and the four surrounding nucleobases c-A, c-T (left, coding strand) and t-T and t-A (right, template strand) for the minimum energy geometry of the complex 2a:DNA.
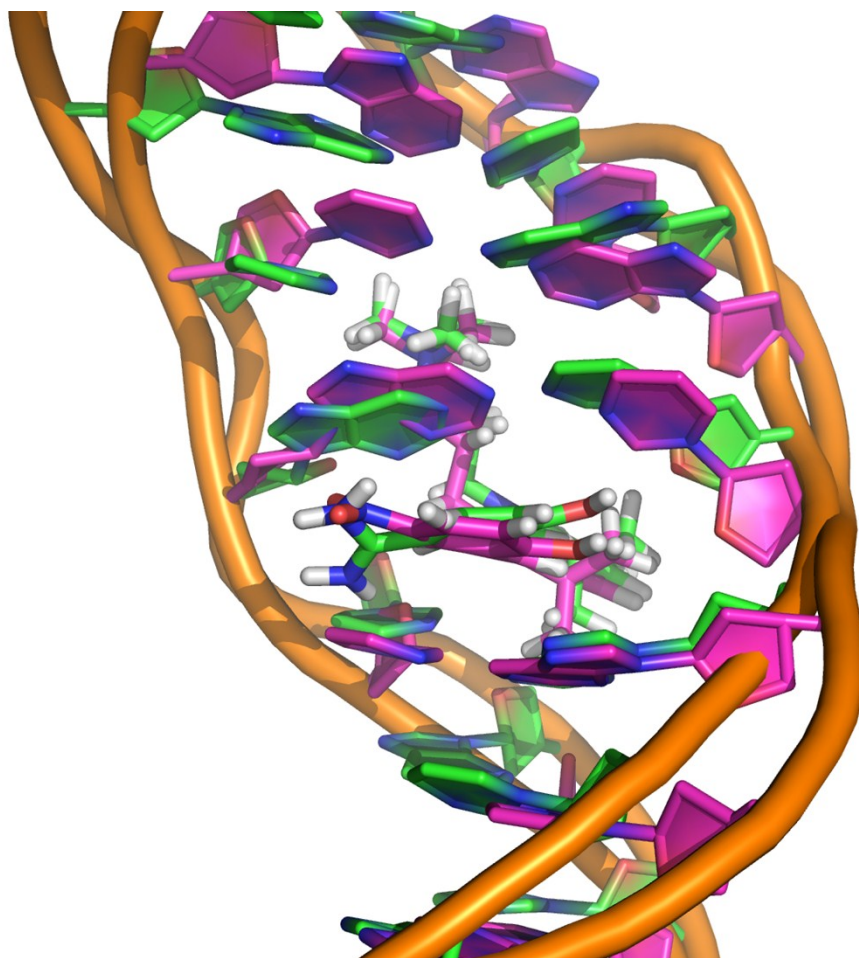
Figure S4. Superimposition of complexes **2a**:DNA (C-atoms colored in pink) and **2b**:DNA (C-atoms colored in green) in their minimum energy geometries.

Table S3. HOMO energies (eV) and electronic delocalization on the c-A, t-A, c-T and t-T of the A-T nucleobases of the DNA duplex in the absence of the intercalative probes **2a** and **2b**. The representative structures were obtained by means of MD simulations and the values were calculated at the CAM-B3LYP/def2-SVP level.

Orbital	Δε (eV)	Delocalization
HOMO	0.00	**c-A**, **t-A**
HOMO-1	-0.34	**t-A**, **c-A**
HOMO-2	-0.76	**t-T**, **c-T**
HOMO-3	-0.78	**c-T**, **t-T**

References

1.   M. Hammarson, J. R. Nilsson, S. Li, T. Beke-Somfai and J. Andréasson, *J. Phys. Chem. B,* 2013, 117, 13561-13571.

2.   M. Hammarson, J. R. Nilsson, S. Li, P. Lincoln and J. Andréasson, *Chem. Eur. J.,* 2014, 20, 15855-15862.