Supporting Information

Electronic Transitions and ESIPT Kinetics of the Thienyl-3-Hydroxychromone Nucleobase Surrogate in DNA Duplexes: a DFT/MD-TDDFT Study

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Figure S1: Distribution of water molecules around M. (A) Radial distribution function g(r) of water molecules with respect to the **M** carbonyl oxygen in solution (black curve). The blue curve describes the variation of the number n of water molecules around **M** with the distance r to the **M** carbonyl oxygen.

Figure S2: Relative energies of **M** conformers obtained fromPBE0-D/ TZVP calculations. The first syn denotes the cyclic O and S heteroatoms on the same side and anti on the opposite. The second syn denotes the OH of 3HC and the deoxyribose on the same side and anti on the opposite.

Figure S3: Root mean square deviation (RMSD) between the structures calculated along a MD trajectory and the MD average structure of **M**-labelled duplexes. **M** is taken in its N ground state and syn-anti conformation. The duplex was obtained by annealing d(CGT TTT **XMX** TTT TGC) with d(GCA AAA **YAbY** AAA ACG), where **Ab** designates an abasic site. (black) **AMA+ TAbT** ; (blue) **TMT+ AAbA**; (red) **CMC+ GAbG**.

Figure S4: Side view of the average structures of 15-mer DNA duplexes containing the **XMX+ YAbY** motif. These structures were obtained from 10ns molecular dynamic trajectories. X= A, T, C; Y= T, A, G, where Ab denote the abasic site. A) **AMA+ TAbT** B) **TMT+ AAbA** C) **CMC+ GAbG.**

Figure S5: Radial distribution functions of the water molecules with respect to the **M** carbonyl oxygen in the ground state, (black) **AMA+ TAbT** ; (blue) **TMT+ AAbA** ; (red) **CMC+ GAbG**.
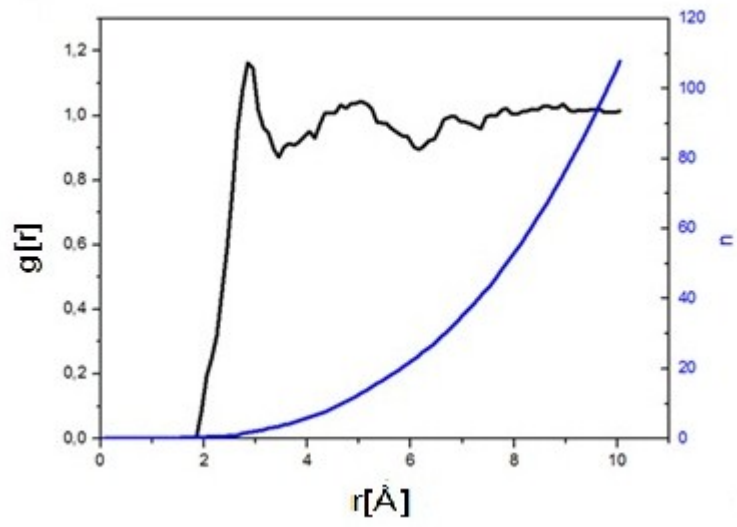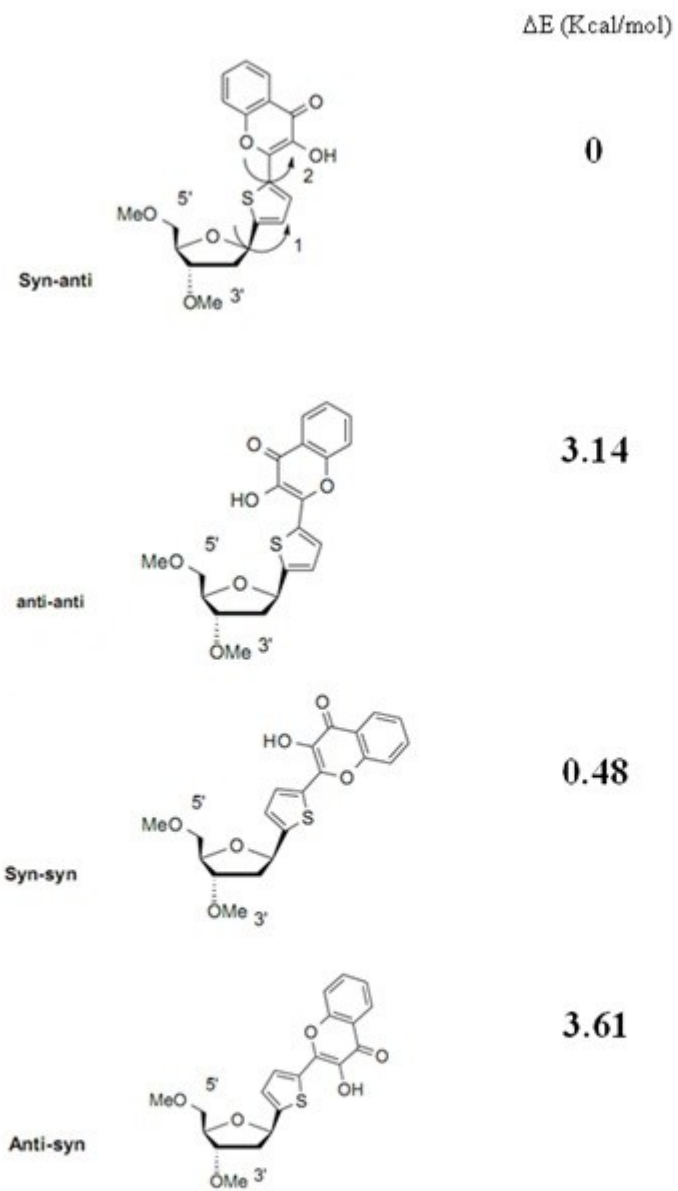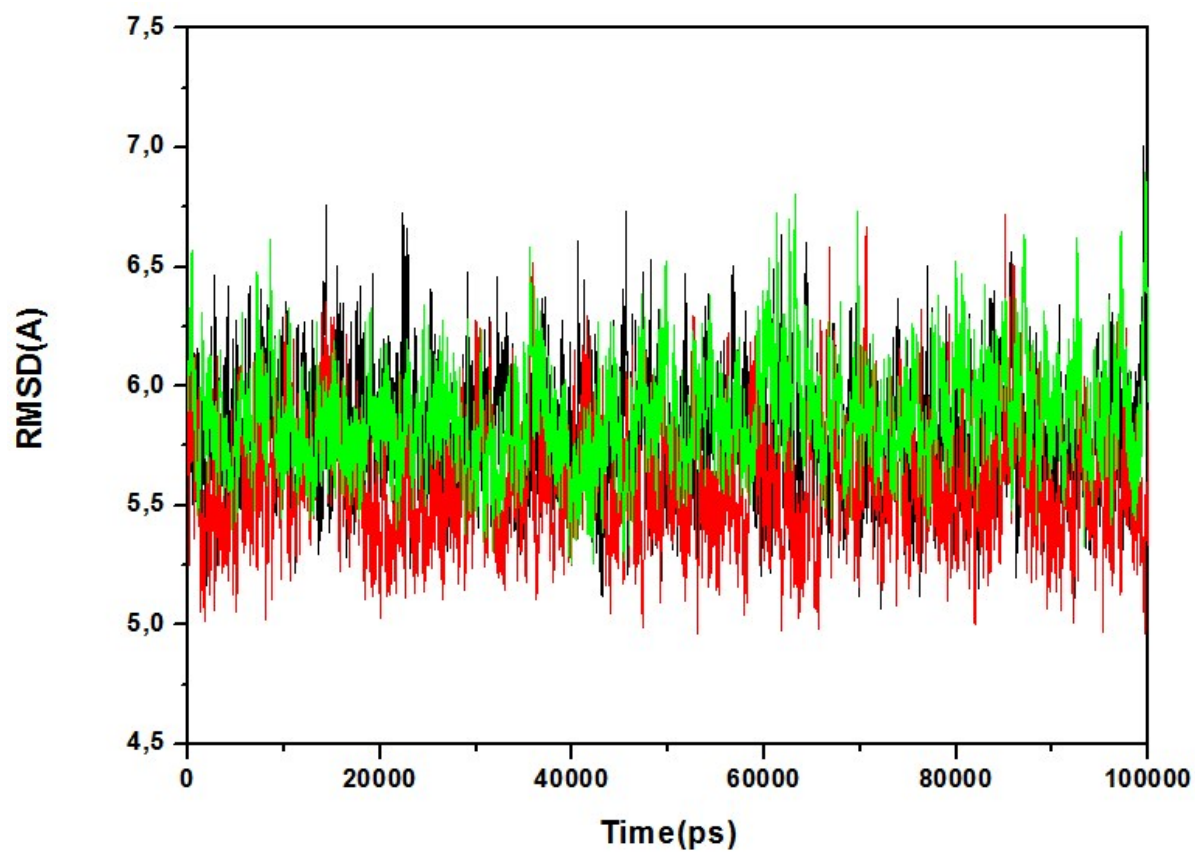
Figure S1

ΔE (Kcal/mol)

0

3.14
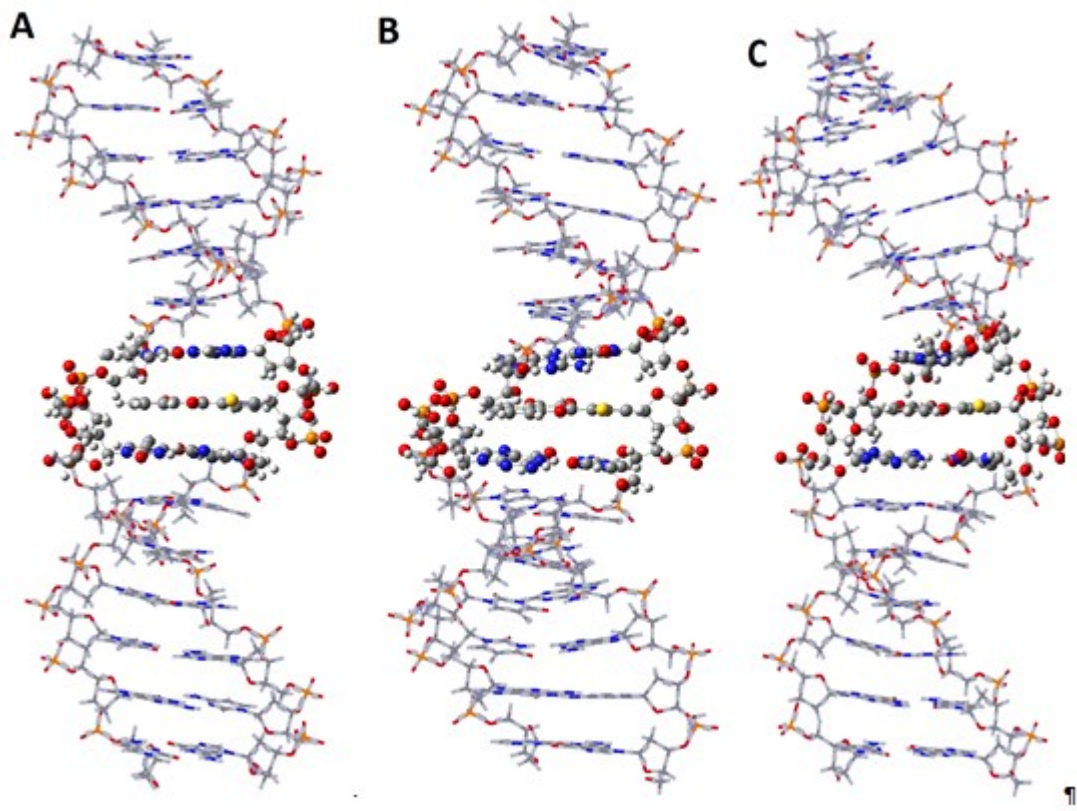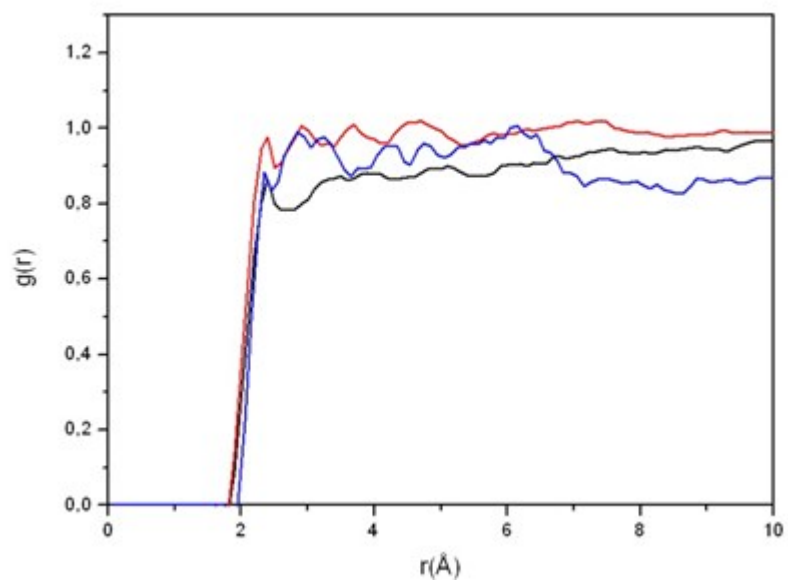
0.48

3.61

Figure S2

Figure S3

Figure S4

Figure S5

Table S1: Bond lengths and angles for **M** in M(H2O)3 complexes. The bond lengths and angles were calculated in the ground state and first relaxed excited state of both the normal and tautomer forms. Calculations were performed by DFT and TDDFT at PBE0-D/TZVP level in bulk water.

Bonds	Bonds Lengths			Angles	Bonds angles		
	S_0	$S_1^N(R)$	$S_1^T(R)$		S_0	$S_1^N(R)$	$S_1^T(R)$
S(1)-C(2)	1.740	1.710	1.751	C(2)-S(1)-C(5)	92	91	92
S(1)-C(5)	1.716	1.765	1.719	S(1)-C(2)-C(3)	111	110	110
C(2)-C(3)	1.380	1.380	1.404	S(1)-C(2)-C(6)	119	118	120
C(2)-C(6)	1.442	1.401	1.402	C(3)-C(2)-C(6)	130	132	130
C(3)-C(4)	1.416	1.397	1.402	C(2)-C(3)-C(4)	113	112	113
C(4)-C(5)	1.369	1.411	1.380	C(3)-C(4)-C(5)	113	113	113
C(6)-O(7)	1.357	1.360	1.363	S(1)-C(5)-C(4)	112	112	112
C(6)-C(11)	1.374	1.424	1.434	C(2)-C(6)-O(7)	112	114	114
O(7)-C(8)	1.353	1.372	1.363	C(2)-C(6)-C(11)	126	127	126
C(8)-C(9)	1.400	1.410	1.413	O(7)-C(6)-C(11)	121	120	120
C(8)-C(12)	1.397	1.382	1.382	C(6)-O(7)-C(8)	121	122	122
C(9)-C(10)	1.455	1.439	1.415	O(7)-C(8)-C(9)	121	122	121
C(9)-C(15)	1.405	1.413	1.417	O(7)-C(8)-C(12)	117	116	117
C(10)-C(11)	1.450	1.462	1.439	C(9)-C(8)-C(12)	122	122	122
C(10)-O(16)	1.243	1.270	1.323	C(8)-C(9)-C(10)	120	120	118
C(11)-O(17)	1.342	1.310	1.272	C(8)-C(9)-C(15)	122	117	118
C(12)-C(13)	1.384	1.401	1.399	C(10)-C(9)-C(15)	119	122	124
C(13)-C(14)	1.405	1.394	1.396	C(9)-C(10)-C(11)	116	115	120
C(14)-C(15)	1.381	1.388	1.386	C(9)-C(10)-O(16)	123	128	119
				C(11)-C(10)-O(16)	121	115	120
				C(6)-C(11)-C(10)	121	121	118
				C(6)-C(11)-O(17)	120	116	122

Table S3: Thermodynamic parameters of the **M**-labelled duplexes calculated along MD trajectories

ΔH is the enthalpy of duplexes bearing **M** in its four mentioned conformations using the MM-PBSA and MM-GBSA methods. Interestingly, the two methods indicated that the most stable duplexes were those with **M** in its syn-anti conformation. The fully matched wild-type duplex and the one containing A opposite an abasic site were analysed for further comparison. Both methods provided the same stability order: ΔH (**XAX+ YTY**; wild type) > ΔH (**XMX+ YAbY**; **M** labelled) >ΔH(**XAX+ YAbY**; non labelled bearing an abasic site), in agreement with experimental observations.[7]

System	ΔH (kcal/mol) (MMPBSA)	ΔH (kcal/mol) (MMGB)
AAA+ TTT	-87.82	-63.61
AAA+ TAbT	-76.59	-57.50
AMA+ TAbTsyn-anti	-80.0	-61.35
AMA+ TAbTanti-anti	-77.7	-58.75
AMA+ TAbTanti-syn	-75.25	-55.35
AMA+ TAbTsyn-syn	-73.48	-55.30
TAT+ ATA	-90.01	-64.55
TAT+ AAbA	-71.66	-58.70
TMT+ AAbA	-83.53	-61.94
CAC+ GTG	-96.56	-72.31
CAC+ GAbG	-89.92	-61.26
CMC+ GAbG	-91.97	-68.73

Table S4: Helical, backbone and groove parameters calculated with the web 3DNA software for **M**-labelled and wild-type sequences. X-disp, Incl, Min-W, shear, stretch and other parameters are defined according to Reference 34.

Base pairs are perpendicular to the helical axis (Incl, Tip $\approx$ 0)[46] and centred on this axis (Xdisp, Ydisp $\approx$ 0). The rise and twist are 3.4-3.7 Å and 36-39°, respectively whether they are evaluated from interbase pair rotation (Rise and Twist) or from translation and rotation with respect to the helical axis (H-rise and H-Twist), in agreement with the standard rise (3.4 Å) and twist (36°) reported for B DNA.[46] The groove parameters are also satisfactorily reproduced, as the major and minor grooves are respectively 10-11.7 Å and 5.1-6.4 Å for the considered duplexes, very close to the standard values of 11.7 Å and 5.7 Å. Lastly, the values of the torsion angles α, β, γ, δ, and ε describing the backbone segments associated with each nucleotide were compared. Among these angles, the most relevant are δ and α describing the torsions of the furanose sugar and the helix turn, respectively. δ range is 120-130°, in agreement with the 70-170° values indicated for B DNA, while α varies between -65 and -70°, in agreement with the experimental values comprised between -41 and -90° for B-DNA. The structural parameters corresponding to wild-type and **M**-labelled DNA are thus very close, indicating that **M** minimally perturbs the conformation of DNA

BP-axis	X-disp	Y-disp	Incl	Tip				
AMA+TAbT	0.21	-0.04	-3.73	-0.46				
AAA+TTT	-0.16	0.11	-0.97	0.38				
Intra-BP	Shear	strech	stagger	Buckle	Propel	Opening		
AMA+TAbT	0.02	-0.02	0.05	0.17	-12.99	-3.04		
AAA+TTT	0.10	0.00	0.07	0.34	-10.94	-3.17		
Inter-BP	shift	Slide	Rise	Tilt	Roll	Twist	H-rise	H-Twist
AMA+TAbT	0.07	-0.06	3.68	0.41	-2.51	39.0	3.38	36.00
AAA+TTT	-0.09	-0.14	3.39	-0.24	-0.68	36.0	3.38	36.00
Backbone	α	β	γ	δ	ε	ξ	χ	Pha	Amp
AMA+TAbT	-65.0	90	60.5	120	-84	-91	-124	125	29
AAA+TTT	-71.0	118	63	132	-80	-101	-130	146	34
Grooves	Min-W	Maj-W						
AMA+TAbT	5.5	10.1						
AAA+TTT	6.3	11.7						

BP-axis	X-disp	Y-disp	Incl	Tip				
BP-axis	X-disp	Y-disp	Incl	Tip				
TMT+AAbA	0.22	0.16	-3.1	-0.36				
TAT+ATA	0.14	0.02	-2.33	0.93				
Intra-BP	Shear	strech	stagger	Buckle	Propel	Opening		
TMT+AAbA	0.16	-0.01	0.09	3.58	-13.43	-2.57		
TAT+ATA	0.19	0.03	-0.03	5.17	-9.8	-4.21		
Inter-BP	shift	Slide	Rise	Tilt	Roll	Twist	H-rise	H-Twist
TMT+AAbA	-0.09	-0.04	3.70	0.19	-2.1	39.40	3.67	39.75
TAT+ATA	-0.08	-0.03	3.39	-0.6	-1.49	36.27	3.38	36.73
Backbone	α	β	γ	δ	ε	ξ	χ	Pha	Amp
TMT+AAbA	-65.0	118	60	121	-114	-93	-124	106	27
TAT+ATA	-70.0	128	64	131	-119	-102	-130	155	35
Grooves	Min-W	Maj-W						
TMT+AAbA	5.6	9.9						
TAT+ATA	6.4	11.6						

BP-axis	X-disp	Y-disp	Incl	Tip				
BP-axis	X-disp	Y-disp	Incl	Tip				
CMC+GAbG	0.33	0.13	-5.4	0.79				
CAC+GTG	0.10	0.09	-2.60	-0.09				
Intra-BP	Shear	strech	stagger	Buckle	Propel	Opening		
CMC+GAbG	0.10	-0.01	0.06	-0.81	-11.40	-2.08		
CAC+GTG	0.10	-0.02	0.09	2.61	-9.8	-2.41		
Inter-BP	shift	Slide	Rise	Tilt	Roll	Twist	H-rise	H-Twist
CMC+GAbG	-0.16	-0.08	3.70	-0.39	-3.27	39.40	3.63	40.0
CAC+GTG	-0.06	-0.06	3.43	0.03	-1.70	36.27	3.43	36.6
Backbone	α	β	γ	δ	ε	ξ	χ	Pha	Amp
CMC+GAbG	-65.0	63	59	123	-114	-96	-124	133	29
CAC+GTG	-69.0	142	63	129	-118	-100	-131	140	34
Grooves	Min-W	Maj-W						
CMC+GAbG	5.1	11.5						
CAC+GTG	6.1	10.2						

Table S5

Maxima absorption λ_{abs} and emission (λ_{N*} and λ_{T*}) wavelengths and corresponding oscillator strengths calculated for the different M conformers in the trimers with TDDFT at the PBE0-D/TZVP level

Structure	λ_{abs} (nm)	f	λ_{N*} (nm)	λ_{T*} (nm)
AMA+TAbTsyn-anti	375	0.53	426	542
AMA+TAbTanti-syn	377	0.50	444	577
AMA+TAbTsyn-syn	377	0.44	425	543
AMA+TAbTanti-anti	382	0.38	420	527