Supporting Information

Reconciling TD-DFT and CASPT2 electronic structure methods for describing the photophysics of DNA

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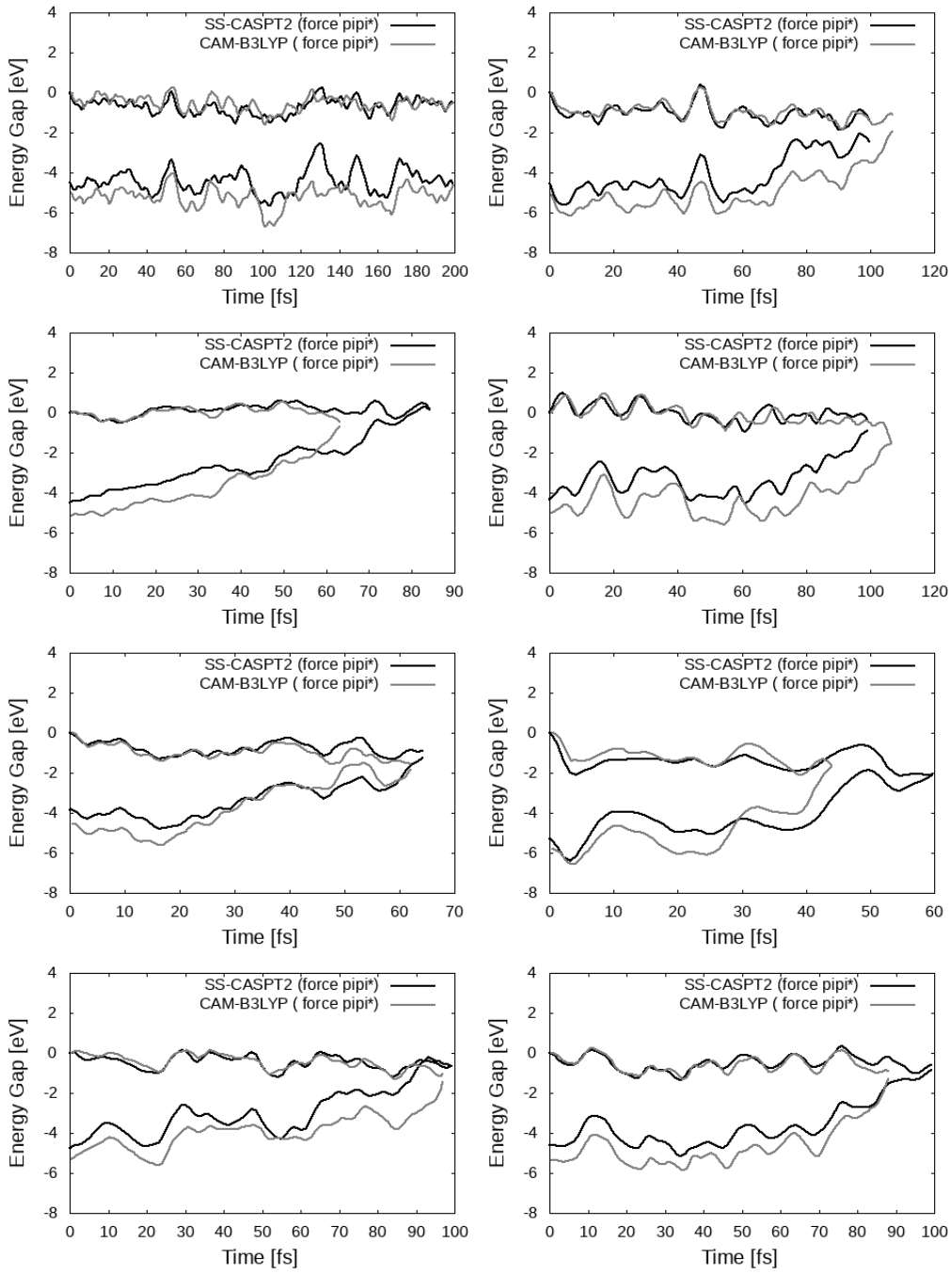
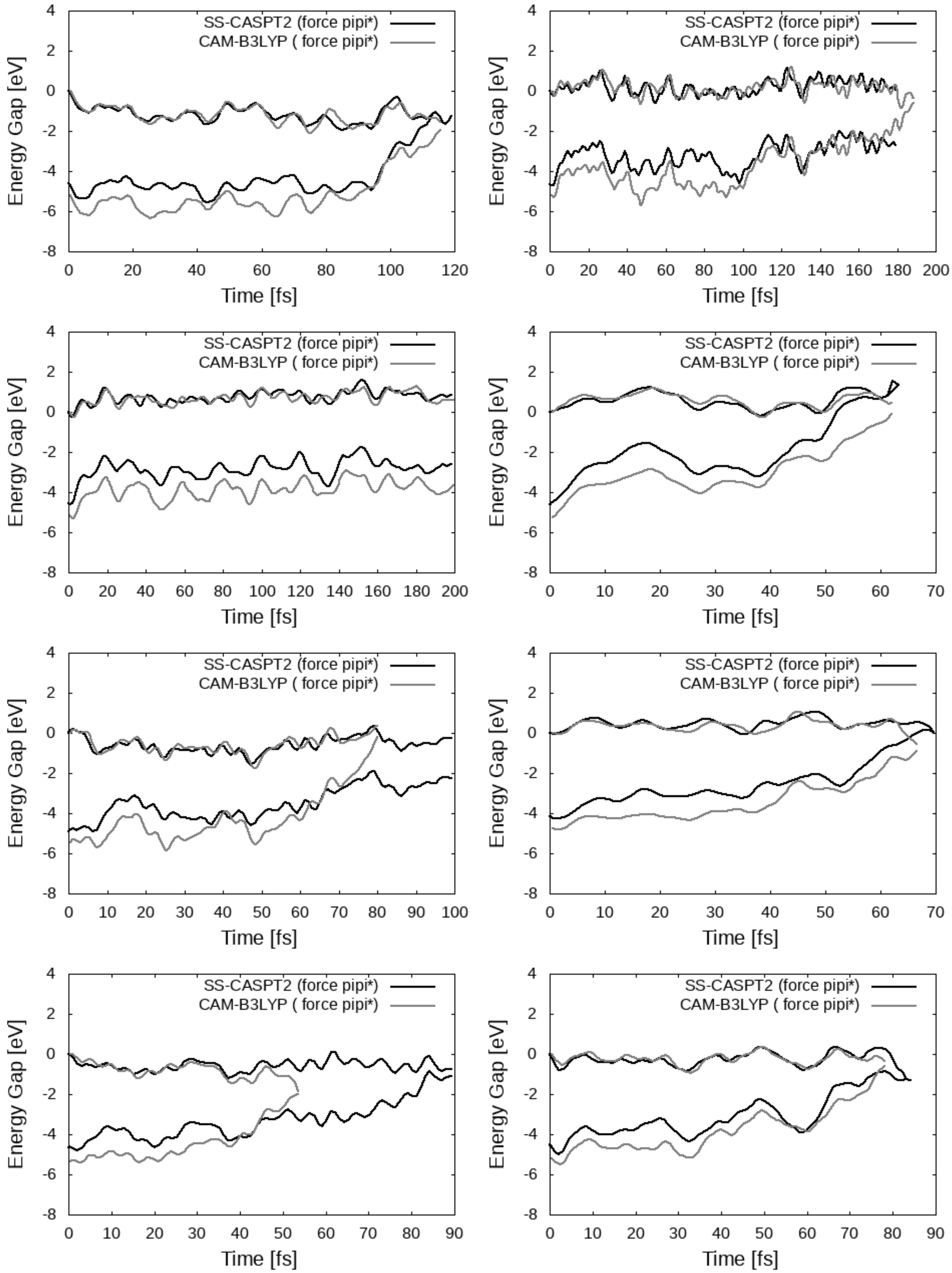
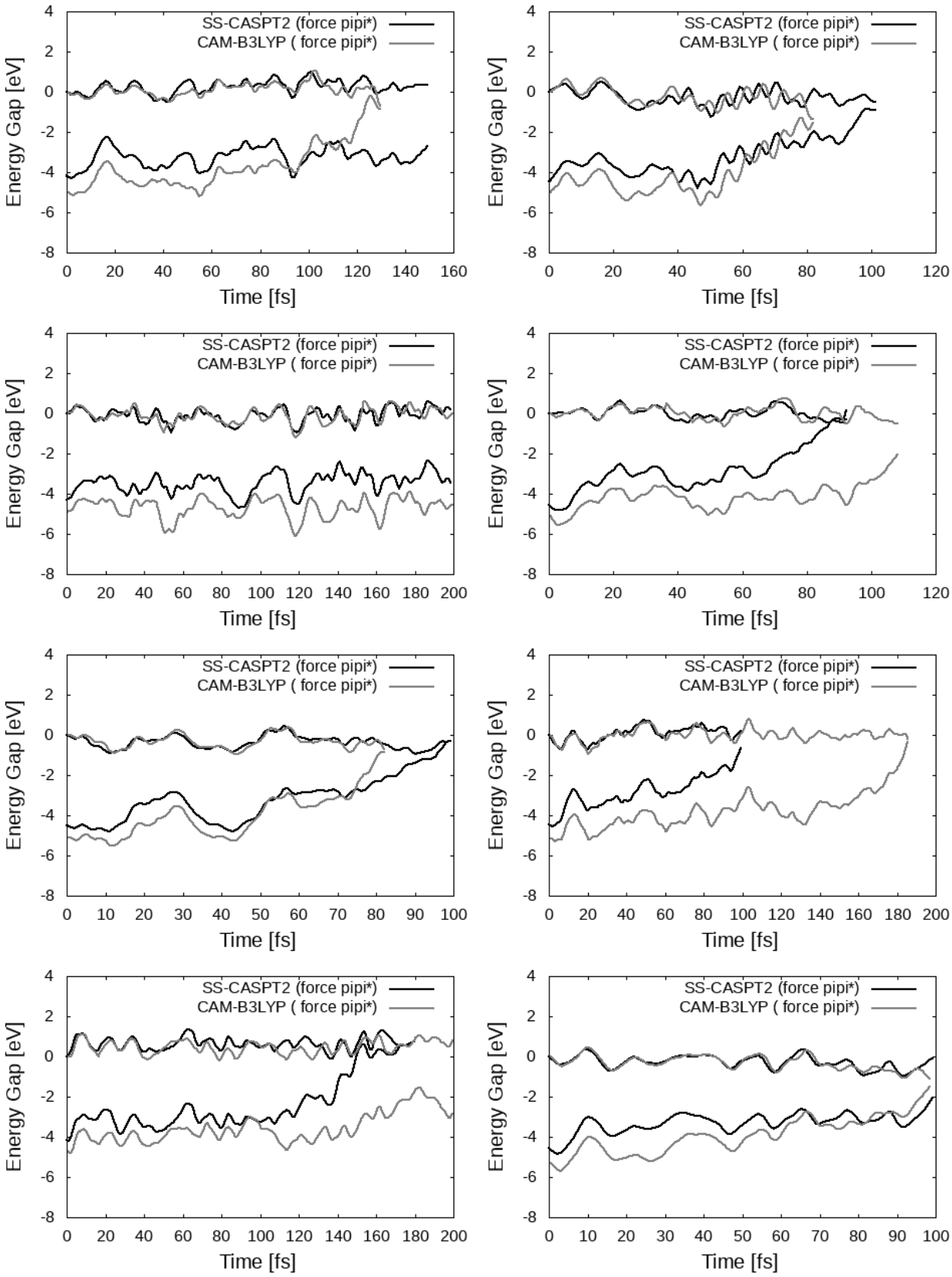
1. The entire set of SS-PT2 and TDDFT trajectories constrained on the ππ* state


SS-CASPT2 (force pipi*)
CAM-B3LYP (force pipi*)
Energy Gap [eV]
Time [fs]


SS-CASPT2 (force pipi*)
CAM-B3LYP (force pipi*)
Energy Gap [eV]
Time [fs]


SS-CASPT2 (force pipi*)
CAM-B3LYP (force pipi*)
Energy Gap [eV]
Time [fs]

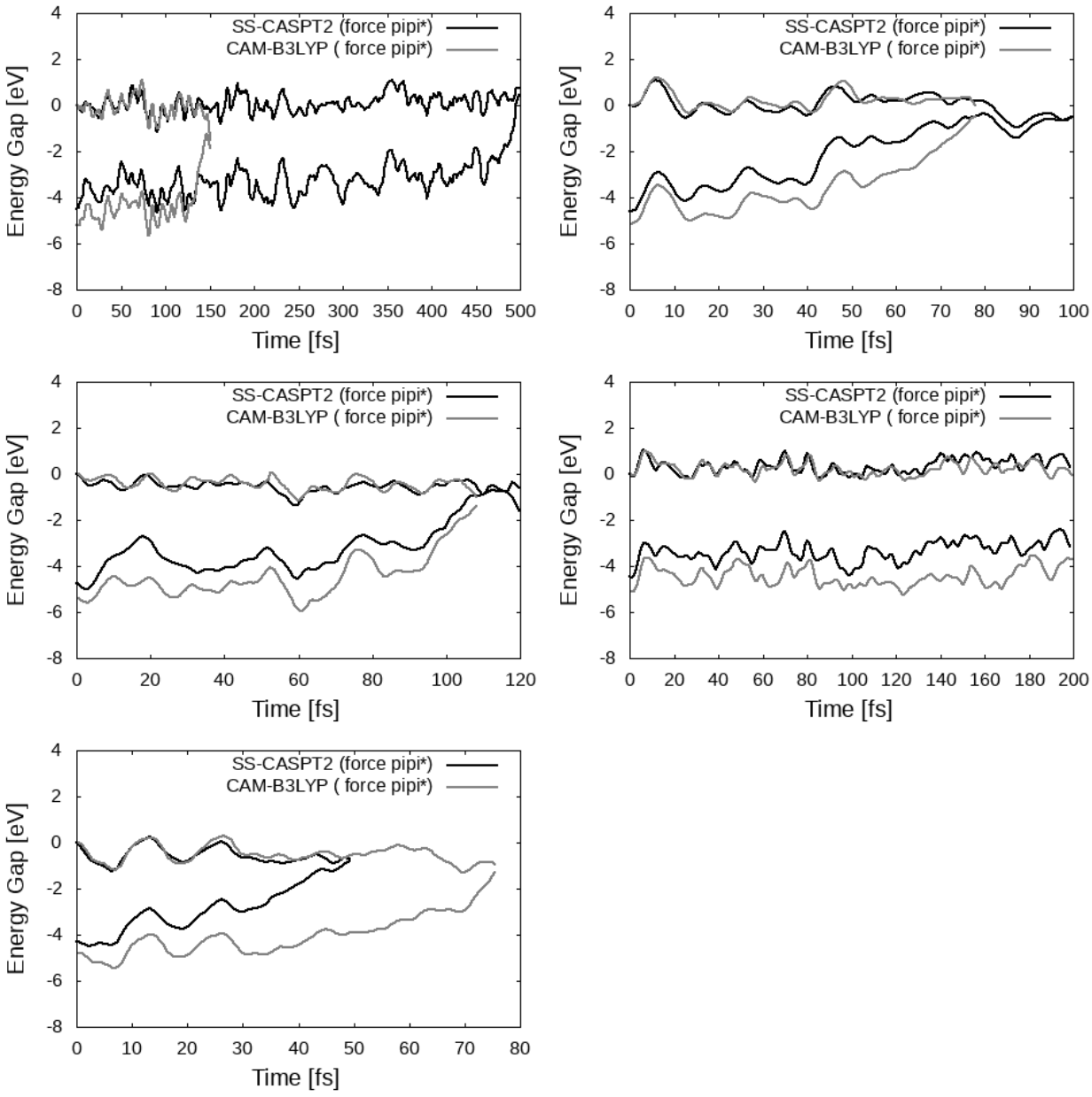


Figure S1. Surafce hopping trajectories of all 29 dynamics constrained on the ππ* state at SS-CASPT2 and TDDFT level.

2. Distribution of vertical transition energies of ππ*/ nπ* at different levels of theory

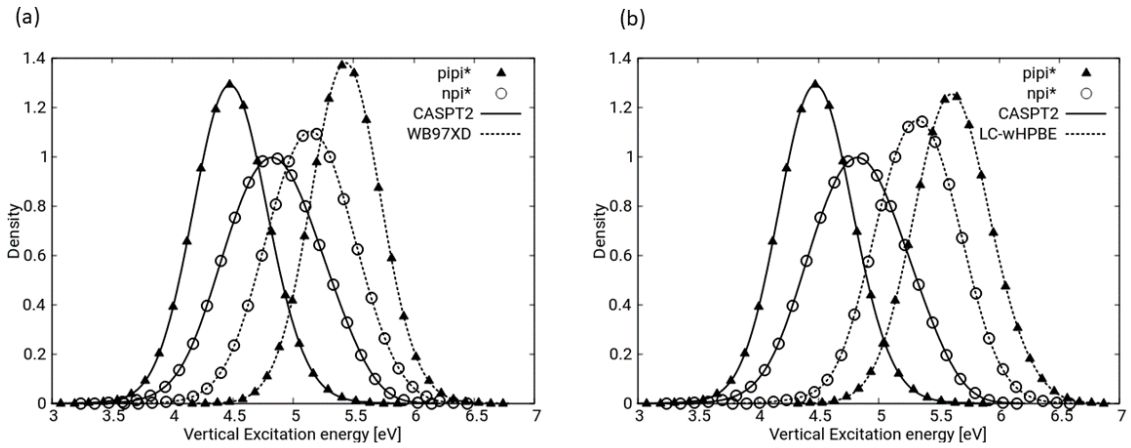


Figure S2. Distribution of vertical transition energies of $\pi\pi^*$ / $n\pi^*$ states for 500 solvated structures in the wigner ensemble for CASPT2 and TDA-DFT in the QM/MM setup for (a) WB97XD and (b) LC-wHPBE

3. QM/MM setup with part of the solvent at QM level

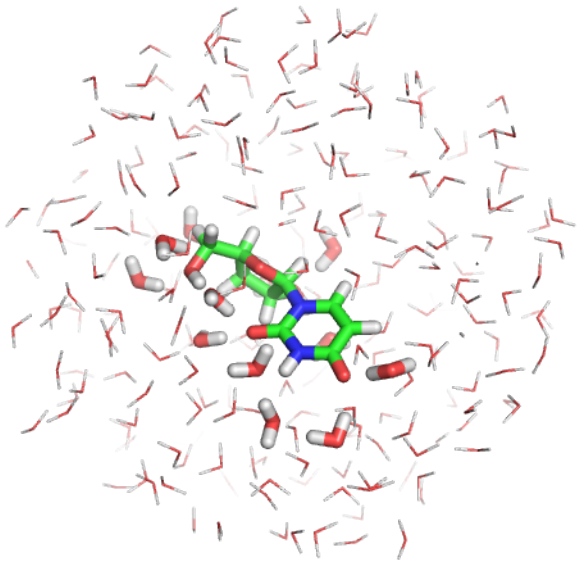


Figure S3. Expanded QM region to include to the nearest solvent water molecules to the nucleotide solute.

4. Franck-Condon energies of the $\pi\pi^*$ and $n\pi^*$ state within polarizable embedding scheme

	M0P1	**M1P1**	**M2P2**
$\pi\pi^*$	5.33	5.35	5.35
$n\pi^*$	5.40	5.49	5.48

Table S1. Energies of the $\pi\pi^*$ and $n\pi^*$ state within polarizable embedding scheme on including higher order multipoles in electrostatic part computed at CAM-B3LYP/cc-pVDZ level at Franck-Condon geometry (optimized at MP2/EEmbedding (TIP3P) level). MnP1 denotes including multipole of nth-order.

5. Solvent parameters for embedding

TIP3P CHARGES

O = -0.834066 , H = 0.417033

SEP CHARGES

O = -0.6744 , H = 0.3372

PEmbedding (MnP1) , n = 0 , 1 or 2

Charges - O = -0.7844, H = 0.3922

Dipole –

O = 0.0000 0.0001 -0.2497

H = 0.0001 0.1484 0.1197

Quadrupole

O = -4.8849 -0.0001 -0.0001 -3.6186 0.0001 -4.2680

H = -0.4963 0.0000 0.0000 -0.1942 0.2560 -0.2964

Polarizability -O = 5.73935 , H = 2.30839

6. Minimum energy path from FC on the ππ* state at XMSPT2 and TDDFT level

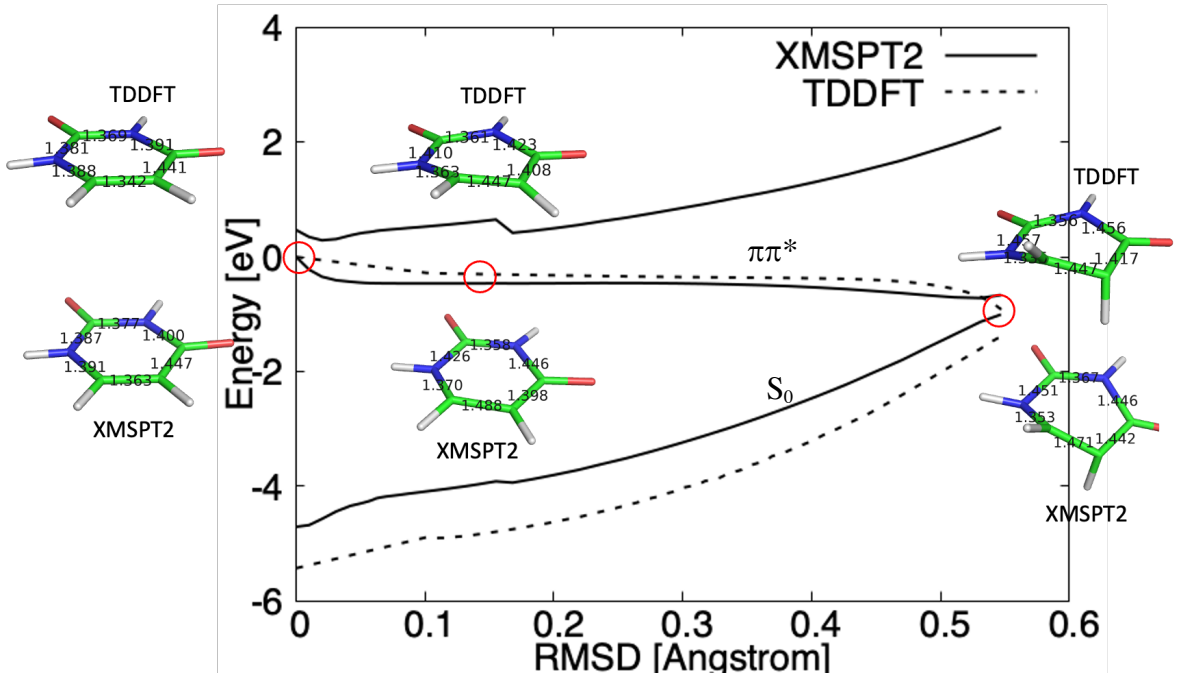


Figure S4. QM/MM Minimum energy path from the FC-optimized structures on the ππ* state calculated at XMSPT2 |14,10| (solid black line)and CAM-B3LYP (dashed lines) level