Supplementary Information

Characterization of the Excited States of

DNA Building Blocks: a Coupled Cluster

Computational Study

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Table S1: Excitation energies (ΔE /eV) and oscillator strengths (f) of the studied excited states of adenine and thymine monomers and dimers in different arrangements, calculated by the CC2 method. In case of monomers, the properties of the monomeric excited states are given for both the third and the fourth fragment, separated by a slash.

		1PLY		WW1	
	State	ΔE /eV	f	ΔE /eV	f
A	$1\pi - \pi^*$	5.568/5.567	0.016/0.017	5.297/5.285	0.049/0.043
	$n - \pi^*$	5.397/5.398	0.001/0.001	5.065/5.097	0.001/0.001
	$2\pi - \pi^*$	5.740/5.740	0.286/0.285	5.458/5.467	0.260/0.266
$(A)_2$	$1\pi - \pi^*$	5.507	0.018	5.154	0.031
		5.529	0.016	5.228	0.020
	$n - \pi^*$	5.326	0.002	4.967	0.001
		5.337	0.000	5.008	0.001
	$2\pi - \pi^*$	5.578	0.027	5.291	0.031
		5.730	0.377	5.416	0.351
T	$n - \pi^*$	4.918/4.910	0.000/0.000	4.771/4.761	0.000/0.000
	$\pi - \pi^*$	5.518/5.521	0.184/0.184	5.415/5.422	0.190/0.189
$(T)_2$	$n - \pi^*$	4.845	0.000	4.668	0.000
		4.847	0.000	4.724	0.000
	$\pi - \pi^*$	5.369	0.107	5.152	0.078
		5.518	0.198	5.394	0.212
A:T	T $n - \pi^*$	5.078	0.000	4.963	0.000
	A $1\pi - \pi^*$	5.517	0.027	5.266	0.050
	T $\pi - \pi^{*\ \dagger}$	5.400	0.142	5.325	0.157
	A $2\pi - \pi^{*\ \dagger}$	5.659	0.291	5.396	0.270
	A $n - \pi^*$	5.630	0.010	5.337	0.000

$\dagger$ Some mixing between these two states can be observed in the WW1 arrangement (see Table S2).

Table S2: Position (POS), participation ratio (PR) and charge transfer character (CT) of the excited states of the A:T Watson-Crick pair in the WW1 arrangement, calculated by the CC2 method.

State	POS	PR	CT
T $n - \pi^*$	1.980	1.042	0.040
A $1\pi - \pi^*$	1.004	1.008	0.008
T $\pi - \pi^* +$ A $2\pi - \pi^*$	1.735	1.639	0.009
A $2\pi - \pi^* +$ T $\pi - \pi^*$	1.241	1.578	0.008
A $n - \pi^*$	1.033	1.071	0.066
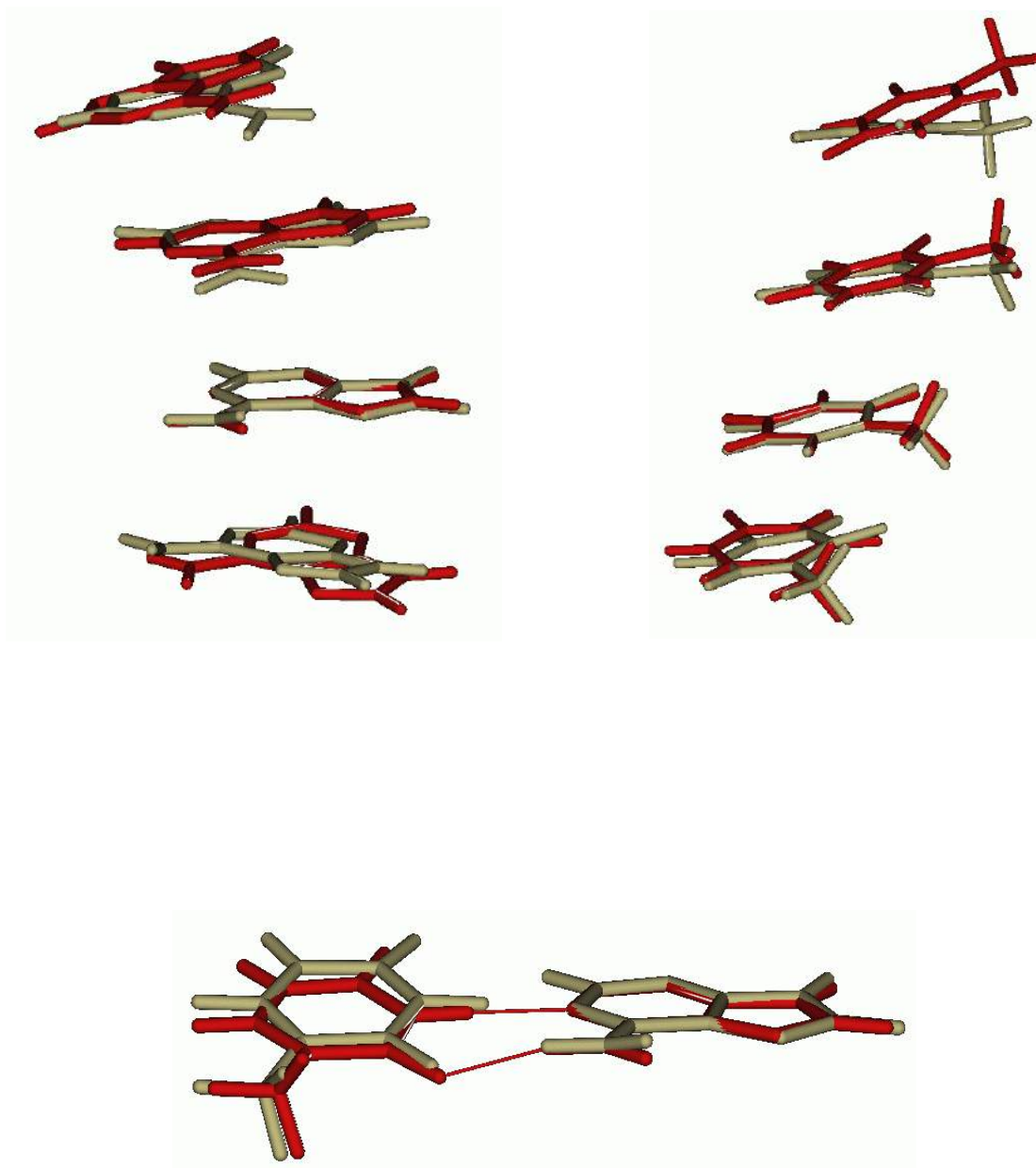
Figure S1: Comparison of the 1PLY (red) and WW1 (brown) arrangements for the AAAA tetramer (upper-left figure), the TTTT tetramer (upper-right figure) and the A:T Watson-Crick pair (lower figure).
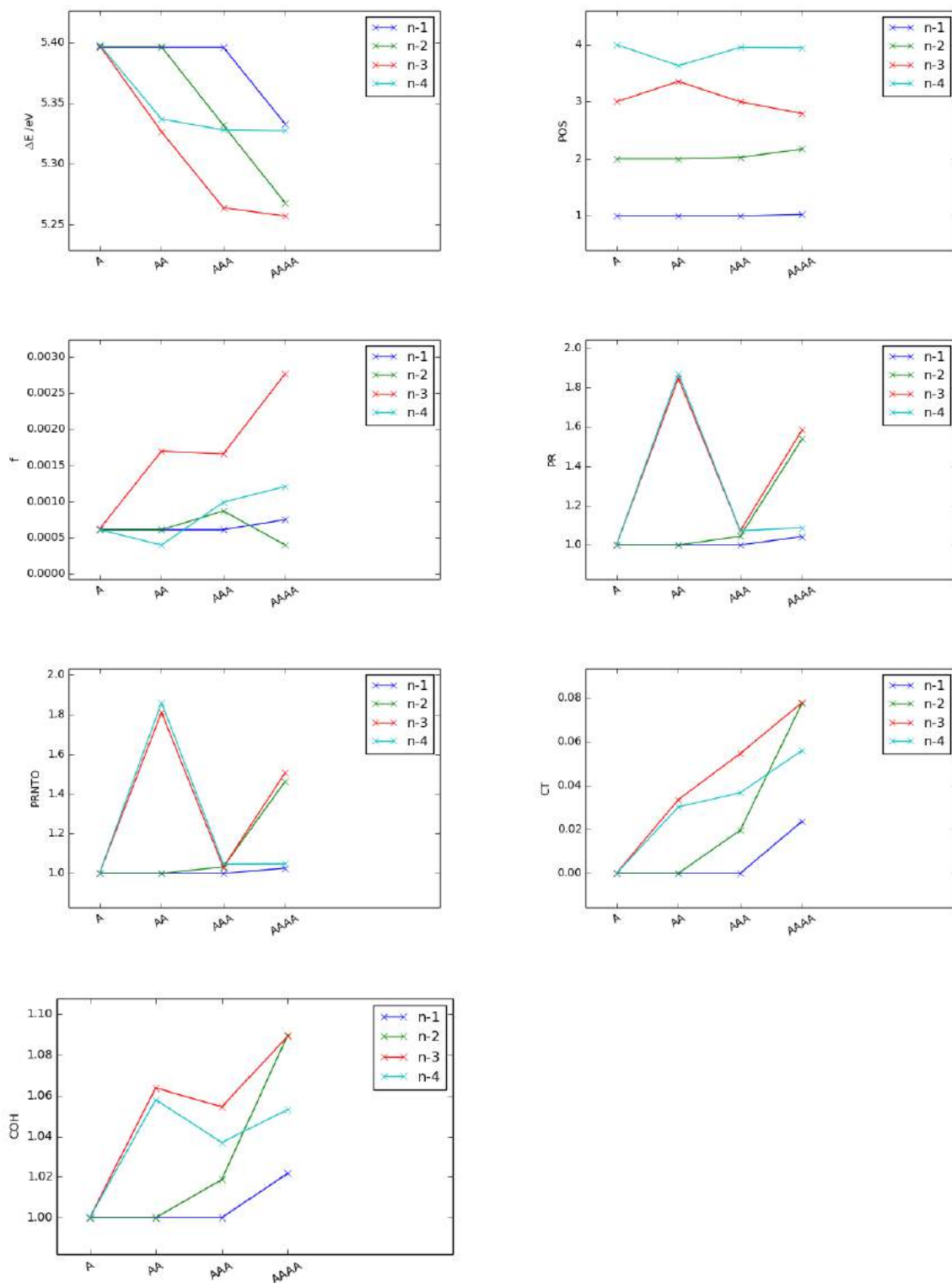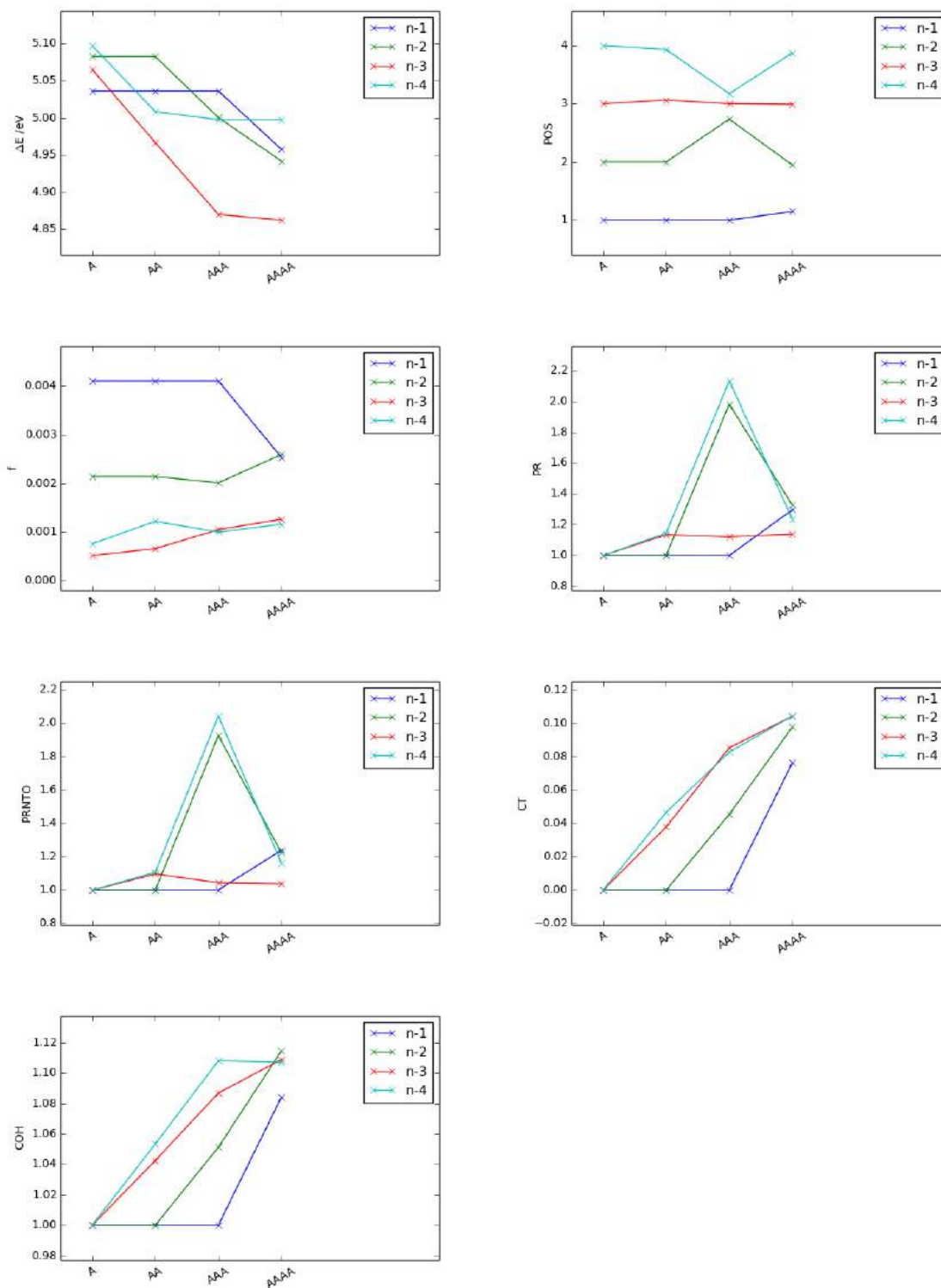
Figure S2: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $n - \pi^*$ states of the poly-A systems at the 1PLY geometry, calculated by the CC2 method.
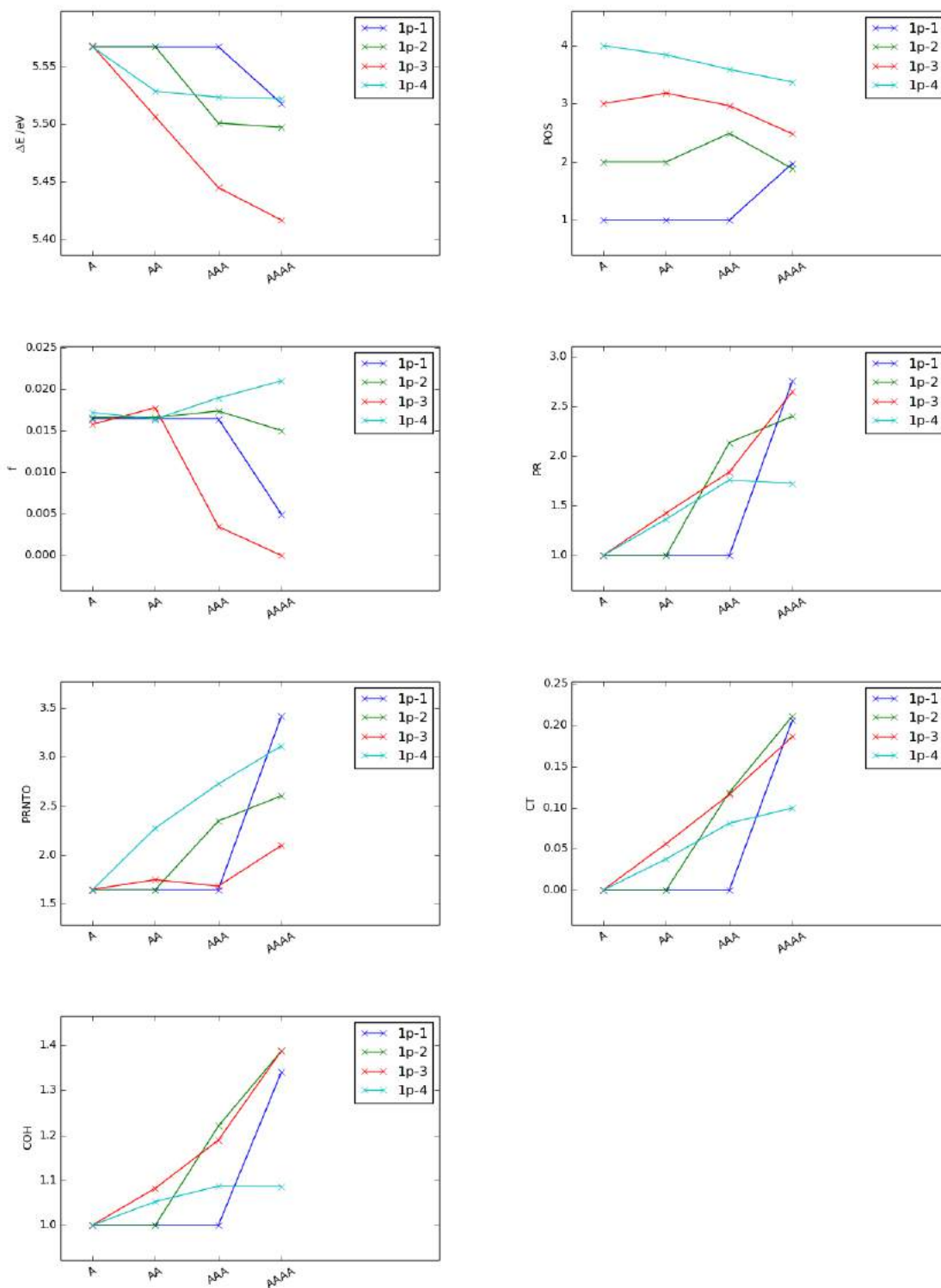
Figure S3: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $n - \pi^*$ states of the poly-A systems at the WW1 geometry, calculated by the CC2 method.
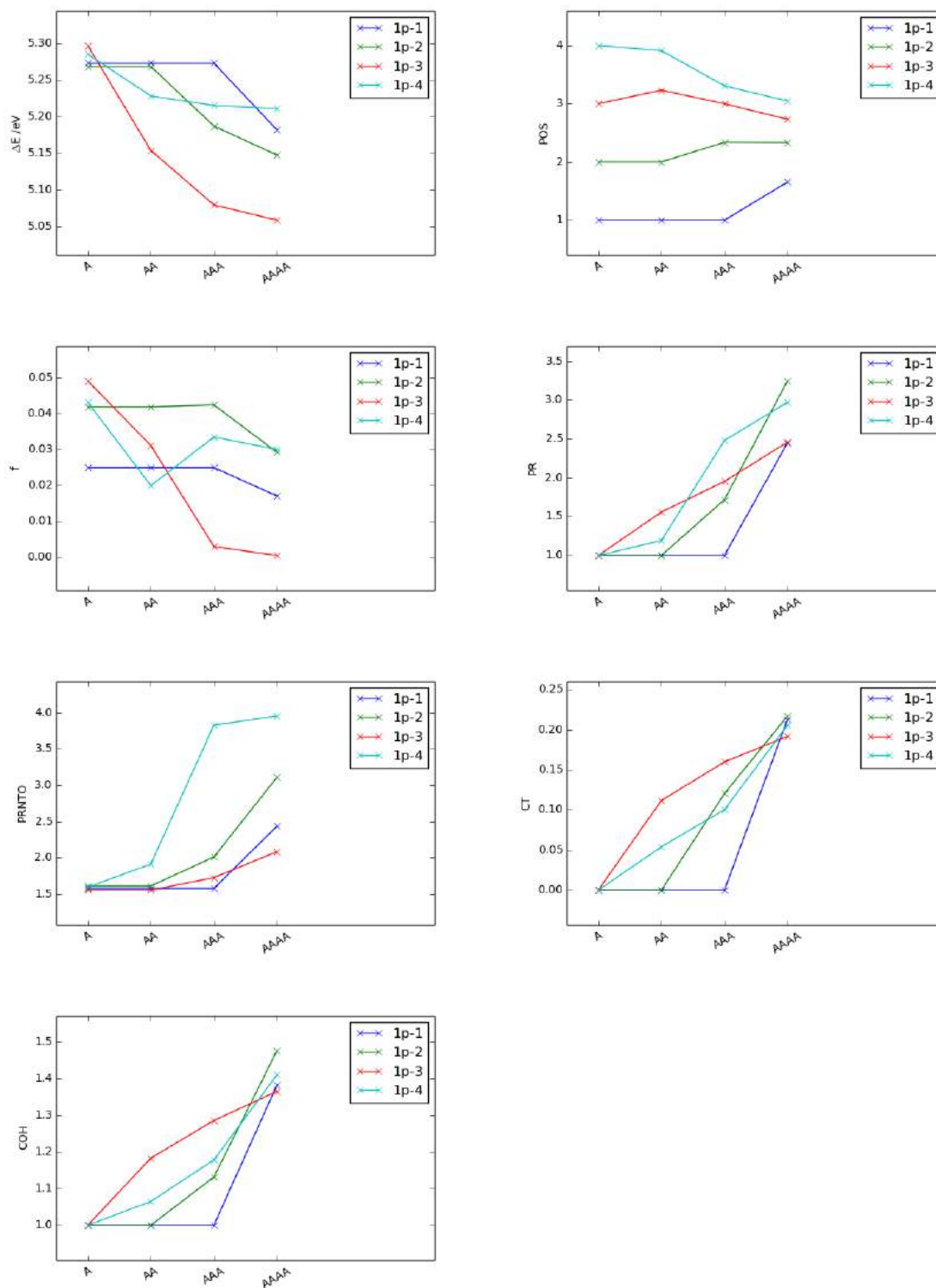
Figure S4: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $1\pi - \pi^*$ states of the poly-A systems at the 1PLY geometry, calculated by the CC2 method.
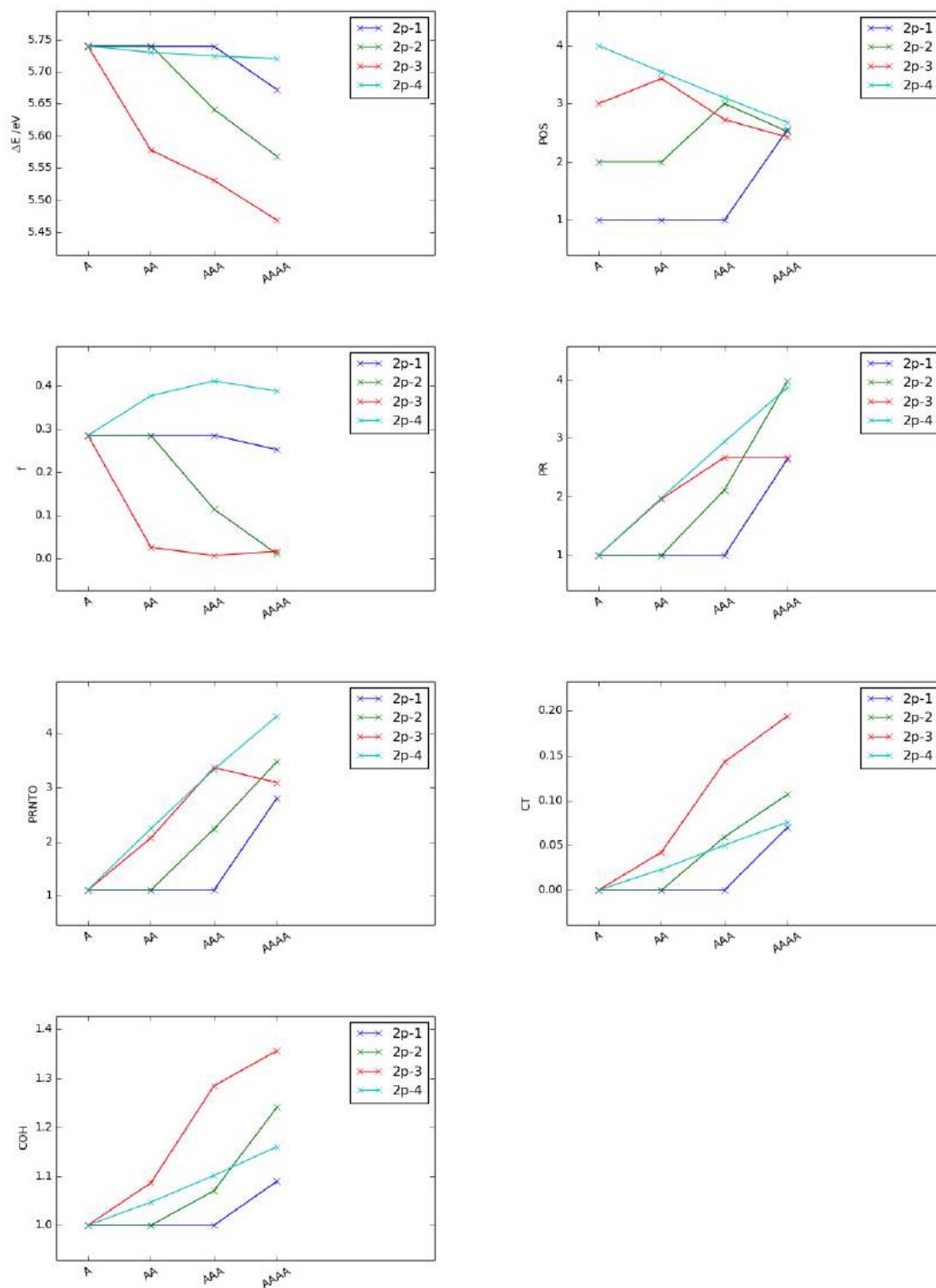
Figure S5: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $1\pi - \pi^*$ states of the poly-A systems at the WW1 geometry, calculated by the CC2 method.
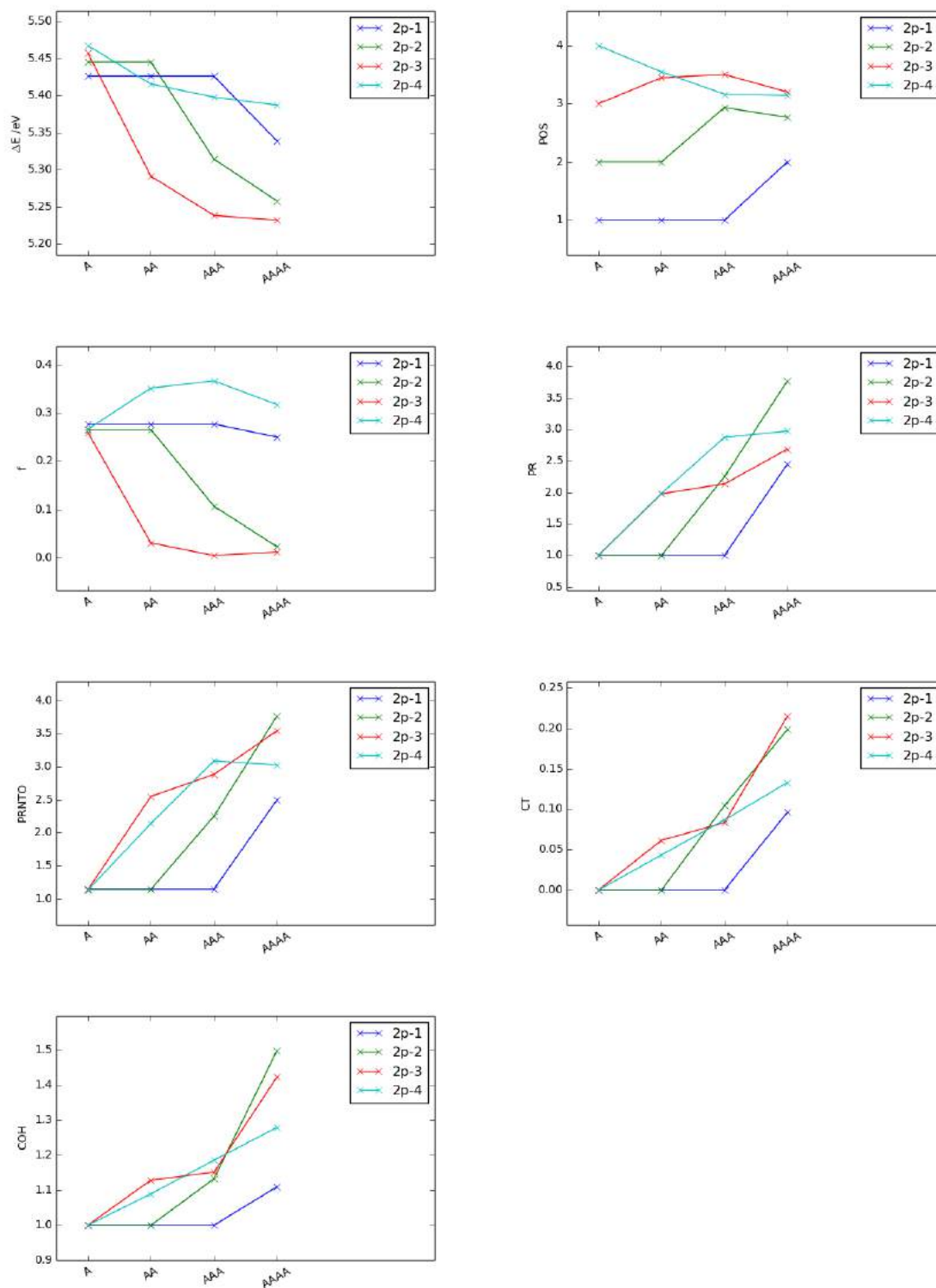
Figure S6: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $2\pi - \pi^*$ states of the poly-A systems at the 1PLY geometry, calculated by the CC2 method.
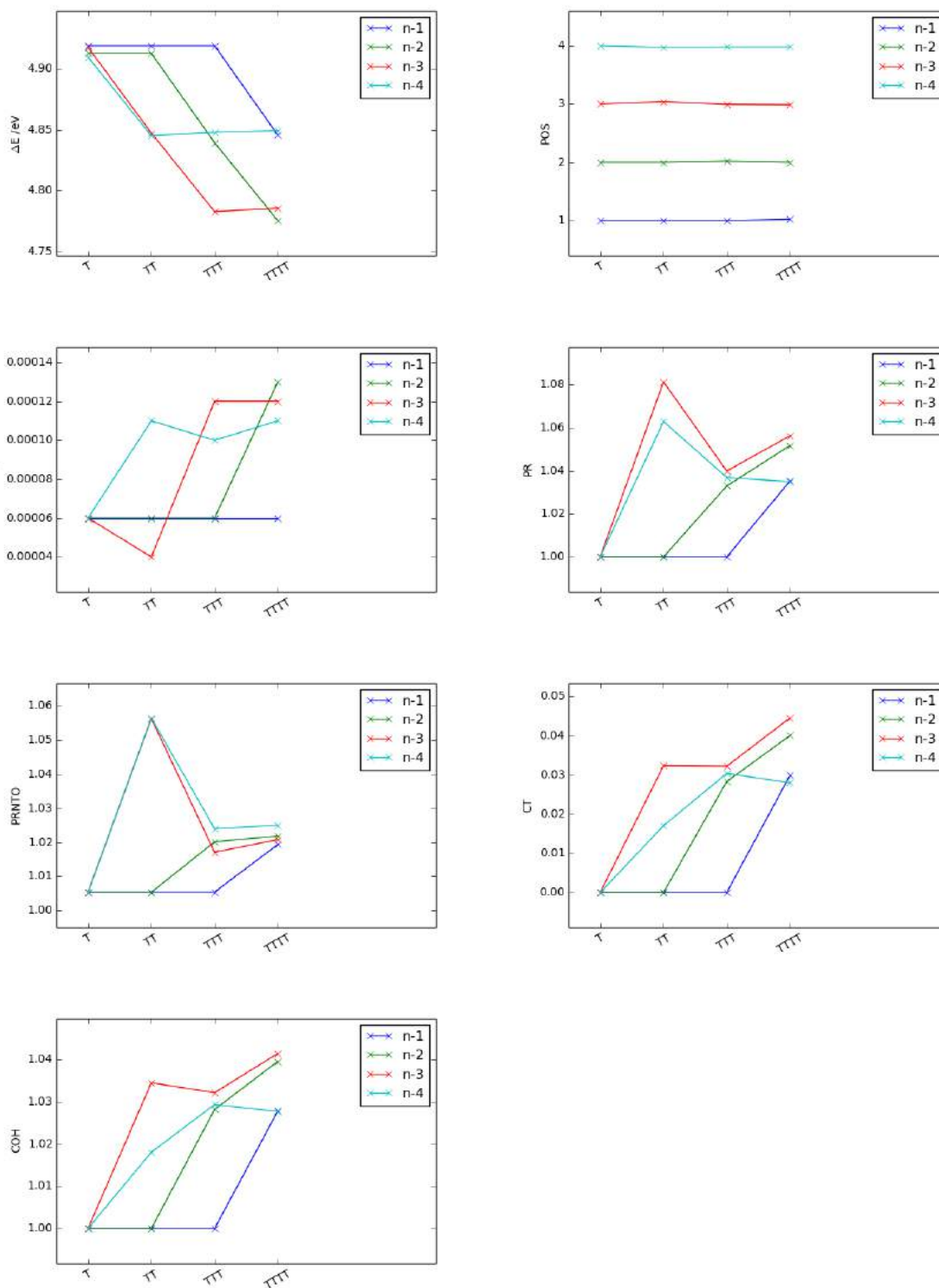
Figure S7: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $2\pi - \pi^*$ states of the poly-A systems at the WW1 geometry, calculated by the CC2 method.

Figure S8: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $n - \pi^*$ states of the poly-T systems at the 1PLY geometry, calculated by the CC2 method.
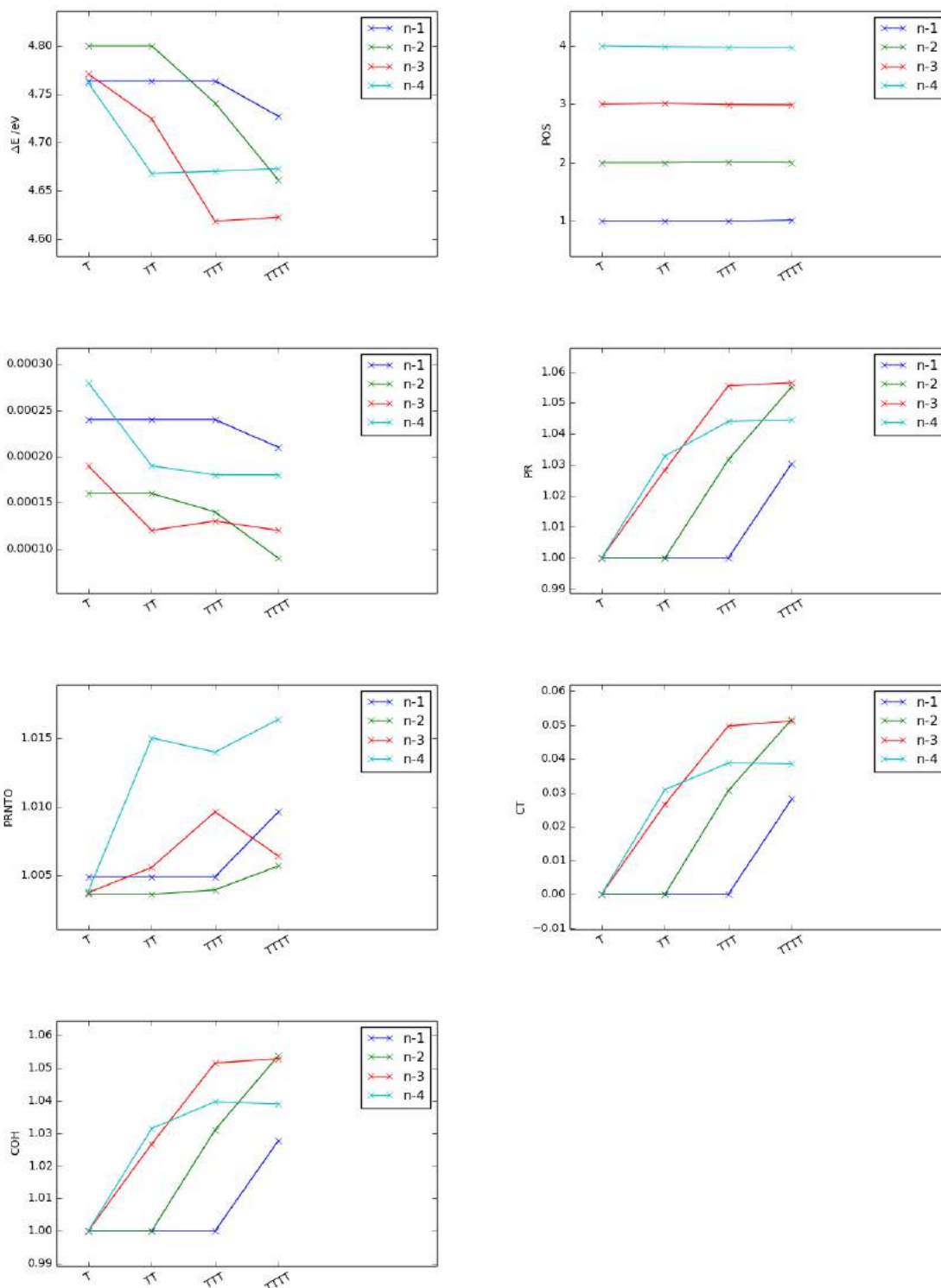
Figure S9: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $n - \pi^*$ states of the poly-T systems at the WW1 geometry, calculated by the CC2 method.
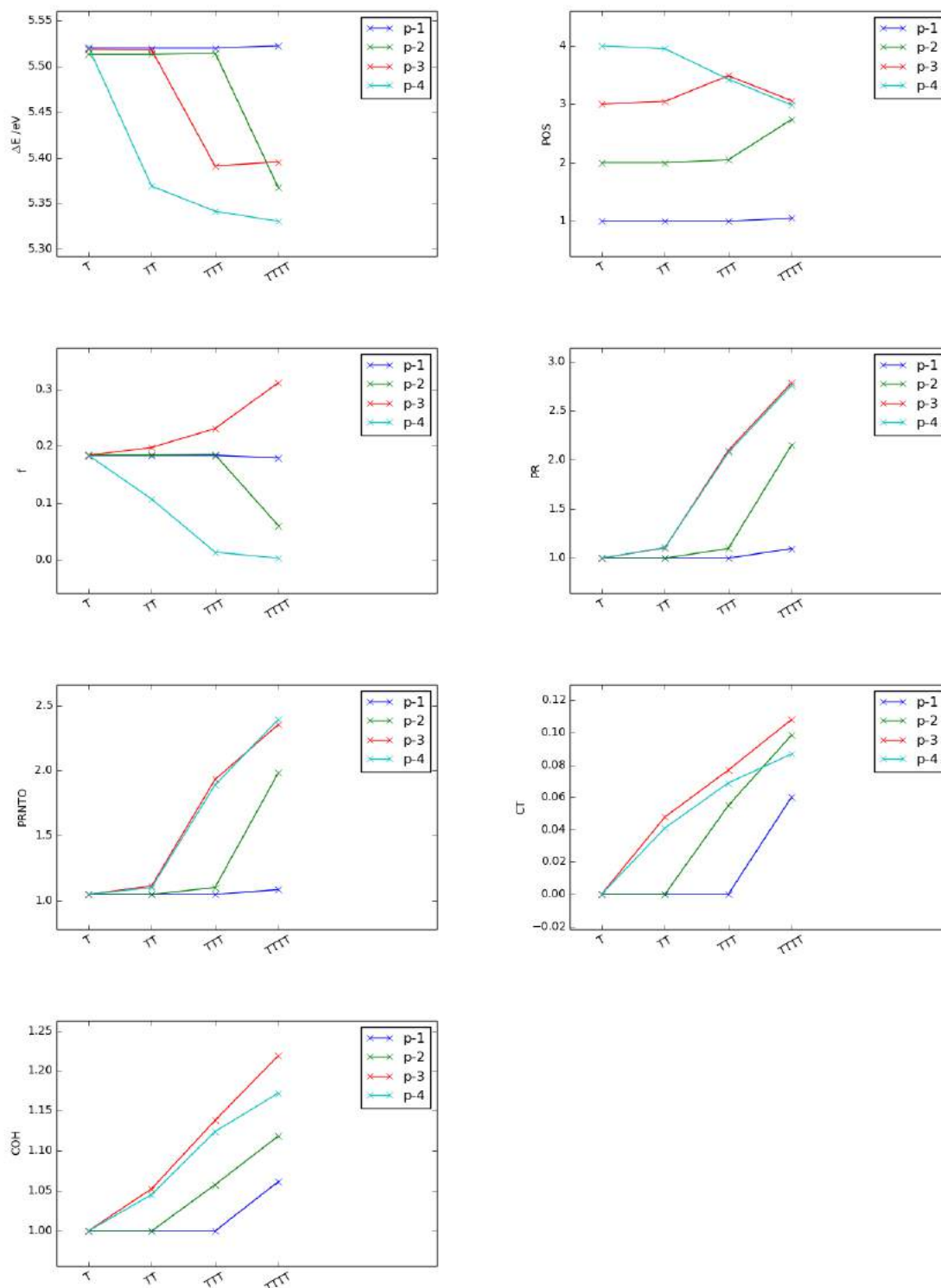
Figure S10: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $\pi - \pi^*$ states of the poly-T systems at the 1PLY geometry, calculated by the CC2 method.
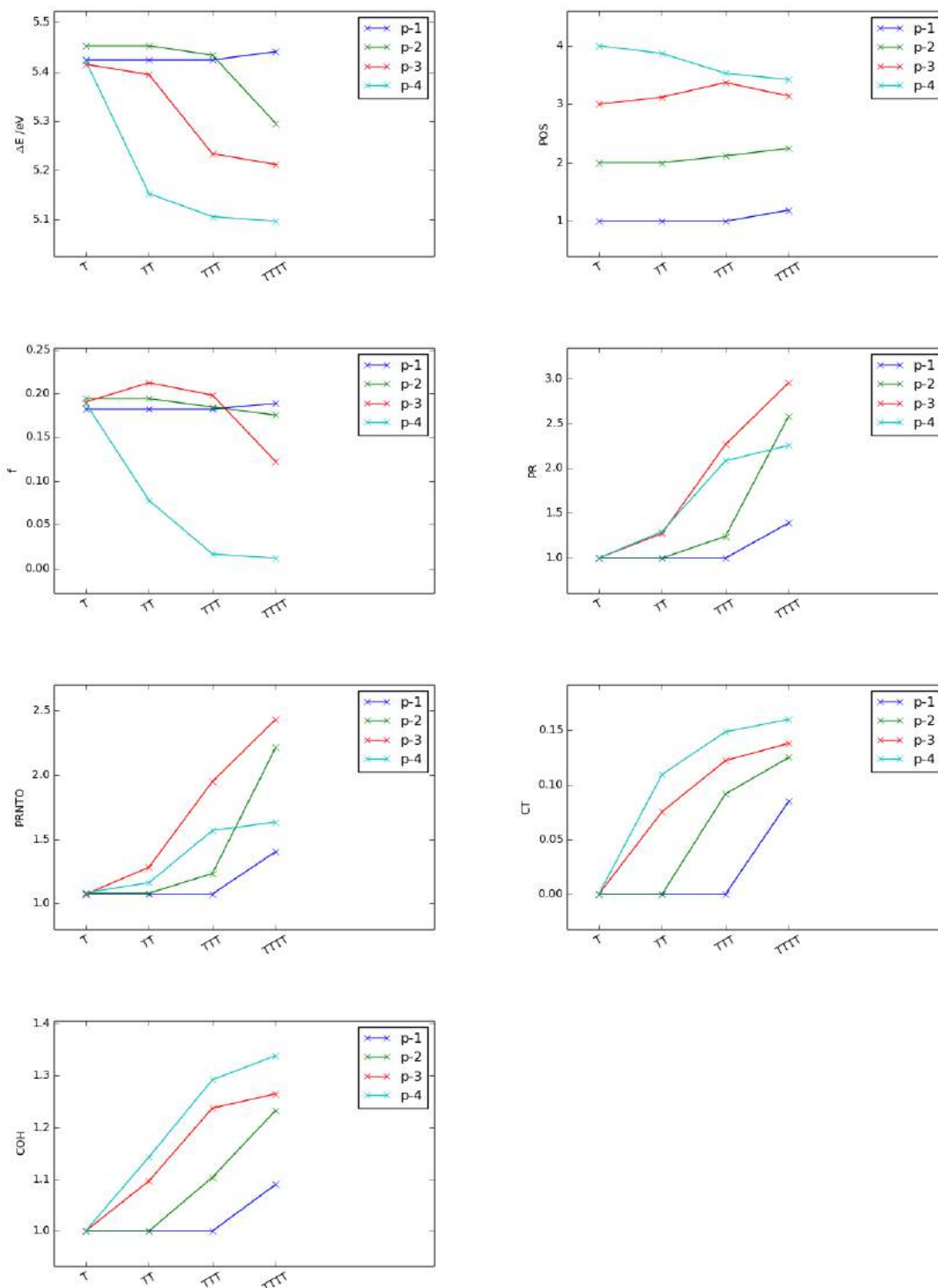
Figure S11: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the $\pi - \pi^*$ states of the poly-T systems at the WW1 geometry, calculated by the CC2 method.
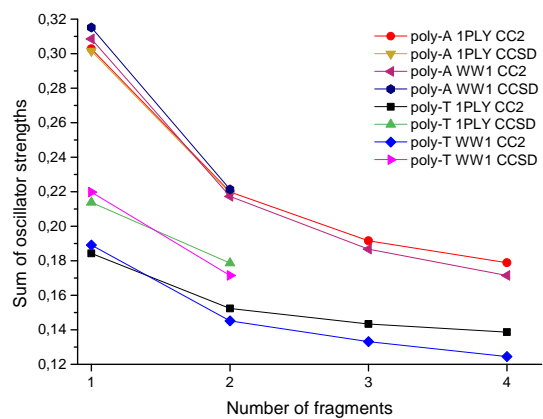
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Figure S12: The sum of oscillator strengths of the studied transitions as a function of fragment number, calculated by CC2 and CCSD methods for single-stranded poly-A and poly-T systems in the 1PLY and WW1 arrangements.
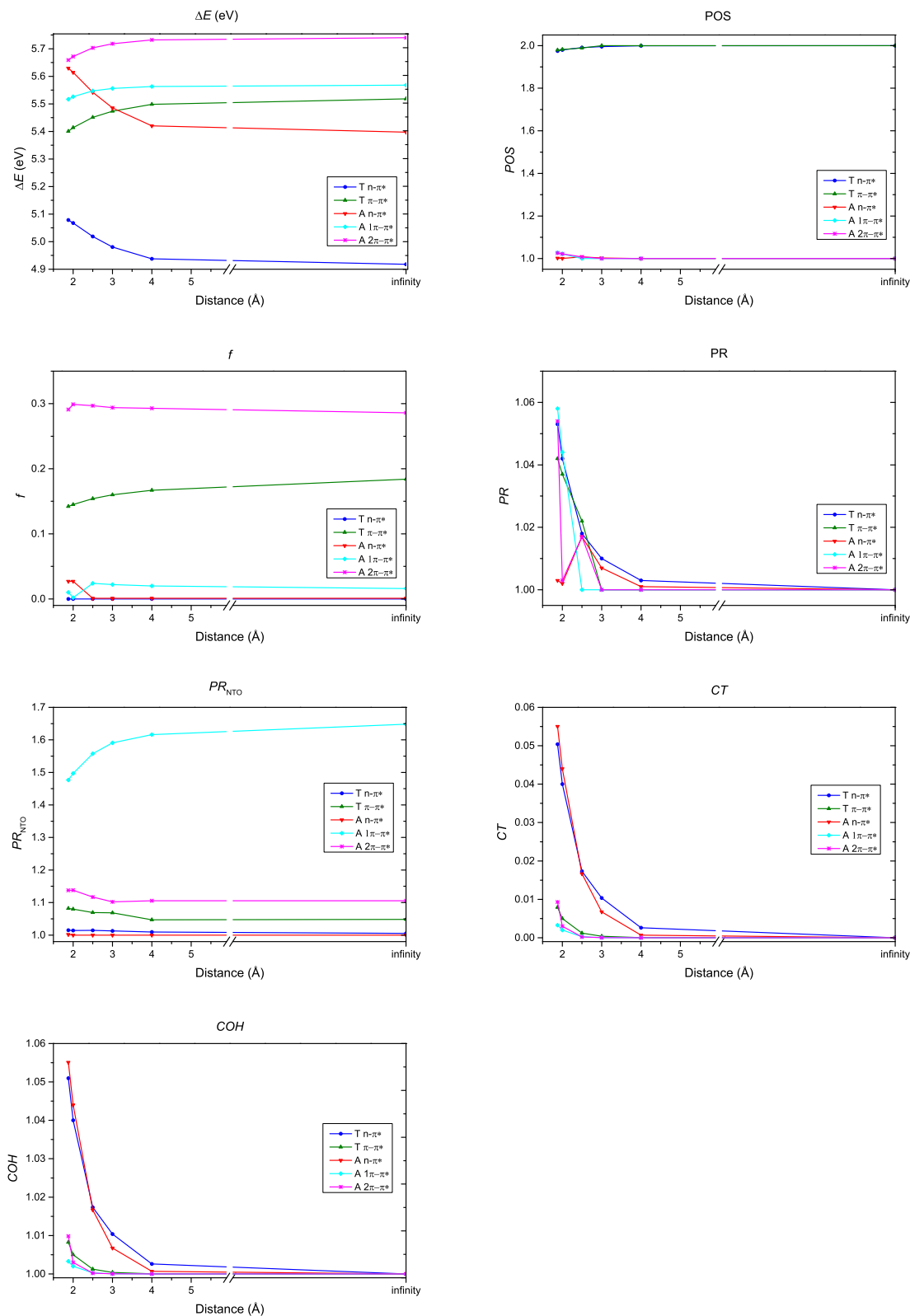
Figure S13: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the excited states of the A:T Watson-Crick pair in the 1PLY arrangement as a function of intermolecular distance, calculated by the CC2 method. The distance between the N3 atom of A and the H3 atom of T is changed without rotating the fragments.
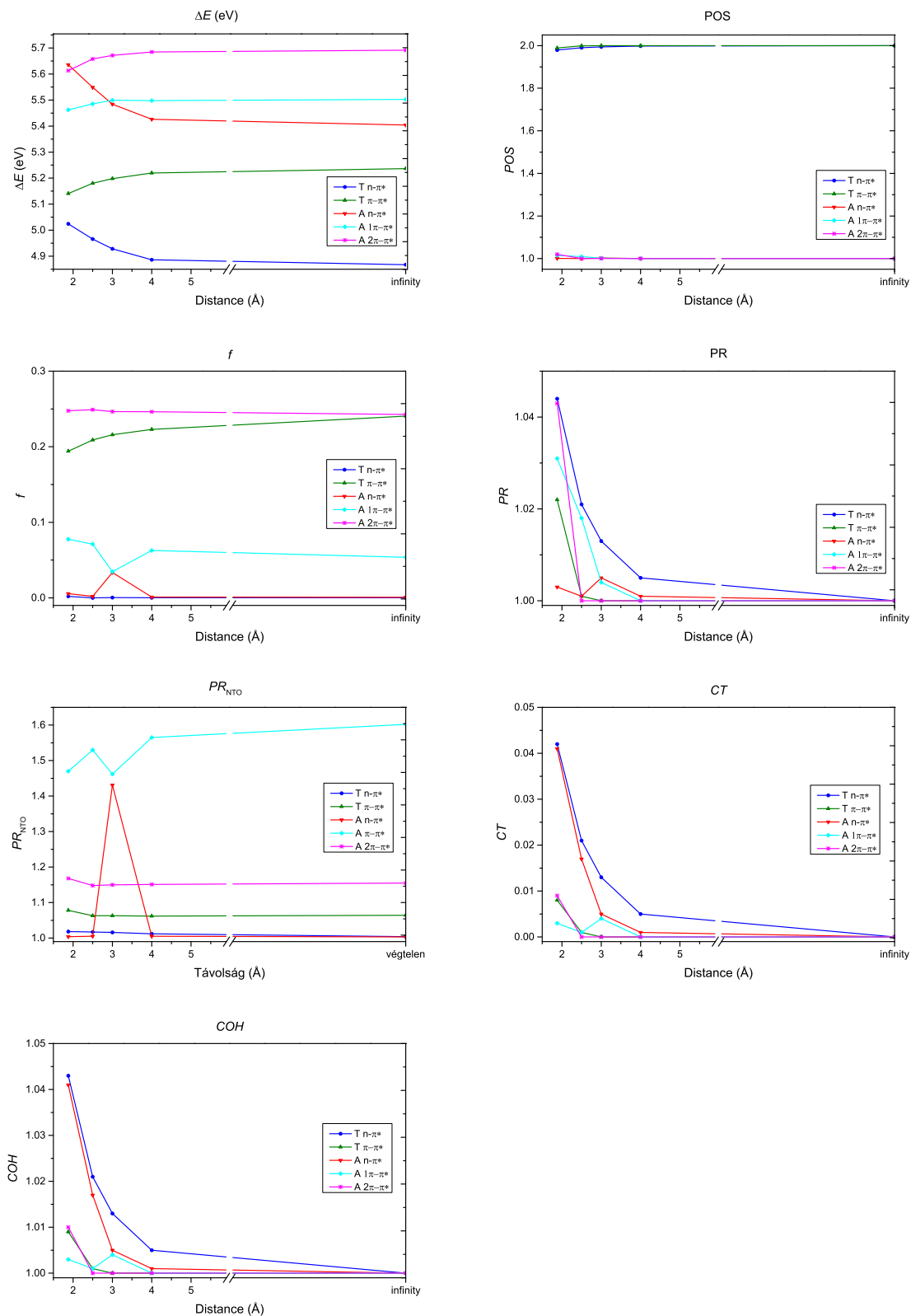
Figure S14: Transition energy (ΔE /eV), position (POS), oscillator strength (f), participation ratio (PR), NTO participation ratio (PR_{NTO}), charge transfer character (CT) and coherence length (COH) of the excited states of the mA:mT Watson-Crick pair in the 1PLY arrangement as a function of intermolecular distance, calculated by the CC2 method. The distance between the N3 atom of mA and the H3 atom of mT is changed without rotating the fragments.
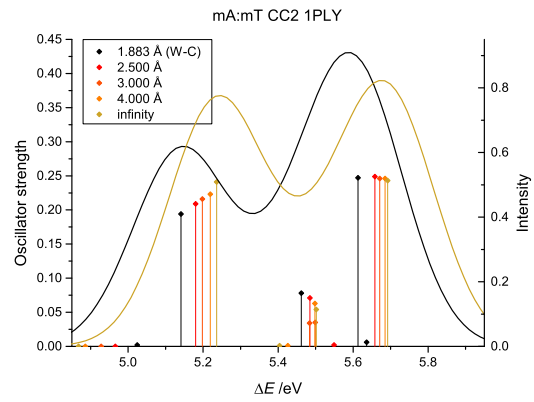
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Figure S15: Simulated absorption spectra of the mA:mT nucleobase pair in the 1PLY Watson-Crick arrangement and in infinite distance, calculated by the CC2 method. Absorption bands are represented by FWHM=0.3 eV Gaussians having area equal to the sum of oscillator strengths of the given system.