Computational Design of the Ring-Expanded Pyrimidine-Based DNA Motifs with Improved Conductivity

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Supporting Information Materials

Table S1. Hydrogen-bond lengths of **G-nC** and **A-nT** (in angstrom, the natural pairs included)

	G-nC			**A-nT**	
	$O_6\cdots H-N_4$	**$N_1-H\cdots N_3$**	**$N_1-H\cdots O_2$**	**$N_6-H\cdots O_4$**	**$N_1\cdots H-N_3$**
Natural	2.834	2.971	2.951	2.952	2.913
x	2.818	2.980	2.937	2.964	2.915
1	2.834	2.969	2.965	2.964	2.910
2	2.832	2.974	2.928	2.934	2.932
3	2.814	2.976	2.910	2.950	2.928
4	2.820	2.976	2.936	2.955	2.917

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Table S2. NMR parameters of WC hydrogen bonds in natural and size-expanded base pairs. All of the NMR parameters were calculated at the B3LYP/6-311+G* level

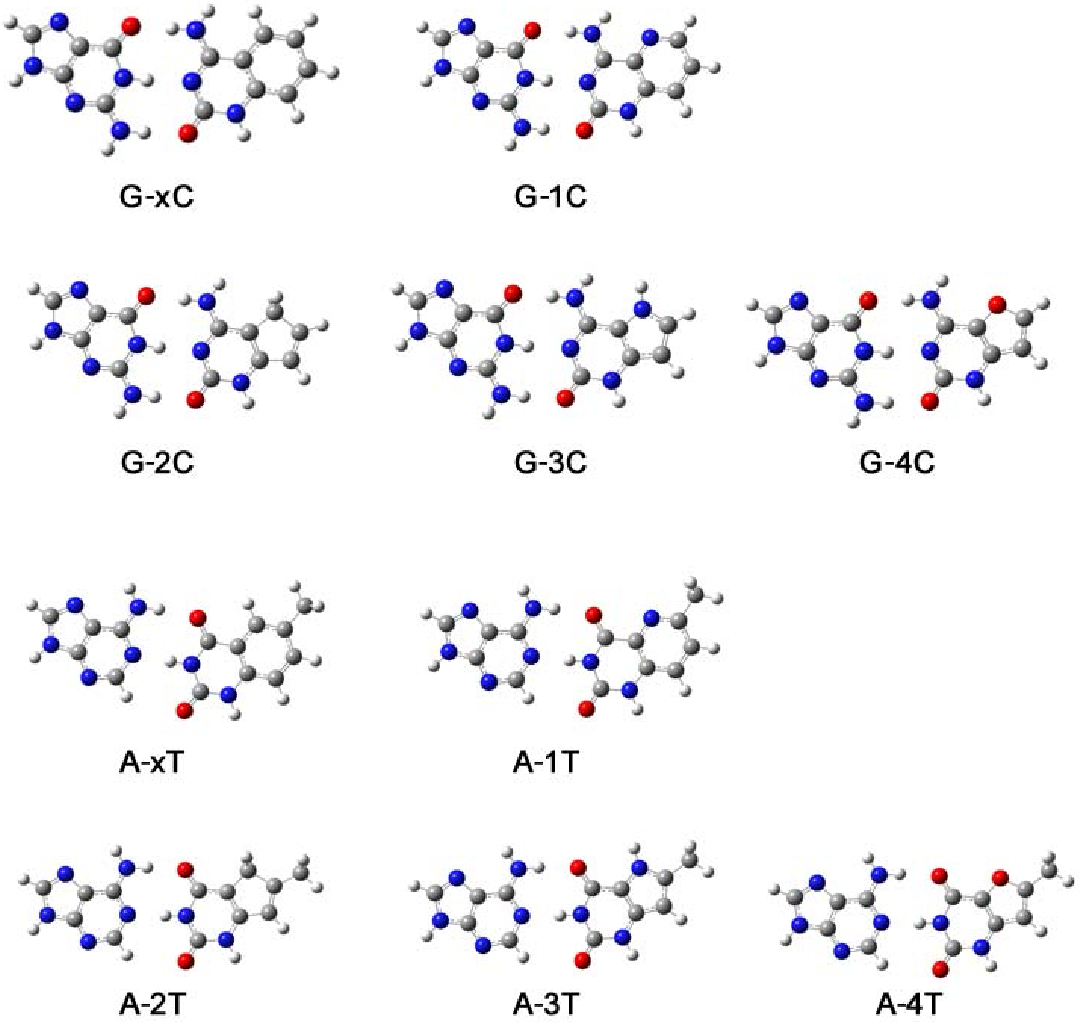
Base pair	Hydrogen Bonds	J_{ON}/ J_{NN}	$\delta(^1H)$	E(2)		$\Delta E_{LP\rightarrow\sigma^*}$	
				E(2) $_{LP(1)\rightarrow\sigma^*}$	E(2) $_{LP(2)\rightarrow\sigma^*}$	ΔE $_{LP(2)\rightarrow\sigma^*}$	ΔE $_{LP(2)\rightarrow\sigma^*}$
G-C	HB(O···H-N)	-5.07	9.6	6.7	12.5	684.0	426.7
	HB(N-H···N)	2.48	11.4	16.9		489.5	
	HB(N-H···O)	-3.38	7.2	3.6	7.8	715.4	445.5
G-xC	HB(O···H-N)	-5.31	10.2	7.4	14.4	652.6	401.6
	HB(N-H···N)	2.41	11.5	16.6		489.5	
	HB(N-H···O)	-3.60	7.4	4.2	8.7	671.4	401.6
G-1C	HB(O···H-N)	-5.08	10.1	7.0	12.0	684.0	426.7
	HB(N-H···N)	2.46	11.5	16.9		489.5	
	HB(N-H···O)	-3.24	7.2	3.6	13.6	709.1	458.0
G-2C	HB(O···H-N)	-5.08	9.6	8.7	18.1	552.2	301.2
	HB(N-H···N)	2.50	11.6	16.3		476.9	
	HB(N-H···O)	-3.68	7.5	4.0	8.5	721.6	445.5
G-3C	HB(O···H-N)	-5.39	9.9	6.9	13.7	677.7	426.7
	HB(N-H···N)	2.48	11.5	17.0		476.9	
	HB(N-H···O)	-3.96	7.7	4.3	9.2	709.1	451.8
G-4C	HB(O···H-N)	-5.37	9.9	7.1	13.1	677.7	426.7
	HB(N-H···N)	2.43	11.4	17.1		476.9	
	HB(N-H···O)	-3.60	7.4	3.8	8.5	715.4	439.3
A-T	HB(N-H···O)	-3.28	8.0	4.1	6.7	715.4	445.5
	HB(N···H-N)	3.24	12.8	21.9		470.6	
A-xT	HB(N-H···O)	-3.15	7.9	4.1	8.2	684.0	414.2
	HB(N···H-N)	3.23	12.9	19.6		508.3	
A-1T	HB(N-H···O)	-3.08	7.9	3.9	6.3	715.4	445.5
	HB(N···H-N)	3.27	13.0	22.6		464.4	
A-2T	HB(N-H···O)	-3.54	8.2	5.8	8.1	690.3	420.4
	HB(N···H-N)	3.07	12.3	20.3		470.6	
A-3T	HB(N-H···O)	-3.36	8.0	4.0	6.4	709.1	439.3
	HB(N···H-N)	3.11	12.3	20.4		476.9	
A-4T	HB(N-H···O)	-3.24	7.8	4.1	6.6	715.4	445.5
	HB(N···H-N)	3.22	12.5	21.7		464.4	

Table S3. Vertical transition energies (scaled by a factor of 0.72), oscillator strengths and assignments of several significant singlet excited-states of the natural and the size-expanded **G-C** and **A-T** pairs. All these results were determined using CIS method

States		E/eV	*f*	Assign.	States		E/eV	*f*	Assign.
G-C	S_1	4.63	0.1115	$\pi_G\pi_G^{*C}$	**A-T**	S_1	4.75	0.2527	$\pi_A\pi_A^*$
	S_2	4.70	0.3263	$\pi_C\pi_C^*$		S_2	4.76	0.2962	$\pi_T\pi_T^*$
	S_4	5.28	0.0012	$n_G^C\pi_G^{*C}$		S_4	4.83	0.0002	$n_T^A\pi_T^*$
	S_5	5.41	0.0014	$n_C^G\pi_C^*$		S_7	5.64	0.0014	$n_A^T\pi_A^*$
	S_{11}	**5.88**	**0.0004**	**$\pi_G\pi_C^*$**		**S_{20}**	**6.60**	**0.0139**	**$\pi_A\pi_T^*$**
G-xC	S_1	3.98	0.1562	$\pi_C\pi_C^*$	**A-xT**	S_1	3.99	0.1316	$\pi_T\pi_T^*$
	S_3	4.64	0.1599	$\pi_G\pi_G^{*C}$		S_3	4.75	0.1837	$\pi_A\pi_A^*$
	S_5	5.21	0.0006	$n_C^G\pi_C^*$		S_5	4.82	0.0005	$n_T^A\pi_T^*$
	S_7	5.30	0.0010	$n_G^C\pi_G^{*C}$		S_8	5.64	0.0013	$n_A^T\pi_A^*$
	S_8	**5.36**	**0.0101**	**$\pi_G\pi_C^*$**		**S_{16}**	**6.12**	**0.0140**	**$\pi_A\pi_T^*$**
G-1C	S_1	3.97	0.2854	$\pi_C\pi_C^*$	**A-1T**	S_1	4.02	0.2265	$\pi_T\pi_T^*$
	S_4	4.63	0.1440	$\pi_G\pi_G^{*C}$		S_4	4.75	0.0000	$n_T^A\pi_T^*$
	S_7	**5.13**	**0.1901**	**$\pi_G\pi_C^*$**		S_5	4.97	0.1594	$\pi_A\pi_A^*$
	S_8	5.16	0.0020	$n_C^G\pi_C^*$		S_9	5.64	0.0015	$n_A^T\pi_A^*$
	S_9	5.28	0.0009	$n_G^C\pi_G^{*C}$		**S_{15}**	**6.29**	**0.0420**	**$\pi_A\pi_T^*$**
G-2C	S_1	3.91	0.2525	$\pi_C\pi_C^*$	**A-2T**	S_1	3.91	0.2780	$\pi_T\pi_T^*$
	S_2	4.64	0.1752	$\pi_G\pi_G^{*C}$		S_2	4.75	0.1784	$\pi_A\pi_A^*$
	S_4	5.28	0.0011	$n_G^C\pi_G^{*C}$		S_4	4.97	0.0003	$n_T^A\pi_T^*$
	S_6	5.45	0.0011	$n_C^G\pi_C^*$		S_7	5.64	0.0011	$n_A^T\pi_A^*$
	S_8	**5.55**	**0.0041**	**$\pi_G\pi_C^*$**		**S_{18}**	**6.29**	**0.0790**	**$\pi_A\pi_T^*$**
G-3C	S_1	4.31	0.4634	$\pi_C\pi_C^*$	**A-3T**	S_1	4.41	0.5414	$\pi_T\pi_T^*$
	S_2	4.64	0.1732	$\pi_G\pi_G^*$		S_2	4.76	0.1383	$\pi_A\pi_A^*$
	S_6	5.49	0.0012	$n_G^C\pi_G^*$		S_4	5.08	0.0002	$n_T^A\pi_T^*$
	S_7	5.30	0.0016	$n_C^G\pi_C^*$		S_8	5.64	0.0010	$n_A^T\pi_A^*$
	S_{14}	**5.87**	**0.0023**	**$\pi_G\pi_C^*$**		**S_{26}**	**6.70**	**0.0087**	**$\pi_A\pi_T^*$**
G-4C	S_1	4.29	0.4231	$\pi_C\pi_C^*$	**A-4T**	S_1	4.41	0.4994	$\pi_T\pi_T^*$
	S_2	4.64	0.1725	$\pi_G\pi_G^{*C}$		S_2	4.75	0.1272	$\pi_A\pi_A^*$
	S_4	5.29	0.0012	$n_G^C\pi_G^{*C}$		S_4	4.95	0.0003	$n_T^A\pi_T^*$
	S_6	5.44	0.0009	$n_C^G\pi_C^*$		S_7	5.64	0.0014	$n_A^T\pi_A^*$
	S_{10}	**5.66**	**0.00113**	**$\pi_G\pi_C^*$**		**S_{20}**	**6.46**	**0.6240**	**$\pi_A\pi_T^*$**

Table S4. Difference value of WC hydrogen bond Lengths (Å) between ground state and electron transfer excited state.

	G-nC			**A-nT**	
	O_6···H-N_4	**N_1-H···N_3**	**N_1-H···O_2**	**N_6-H···O_4**	**N_1···H-N_3**
Natural	-0.021	-0.019	-0.006	-0.030	-0.010
x	-0.023	-0.020	-0.016	-0.039	-0.017
1	0.007	-0.013	-0.015	-0.015	0.006
2	-0.018	-0.014	0.011	-0.027	-0.012
3	-0.042	-0.019	-0.017	-0.033	-0.014
4	-0.021	-0.009	-0.024	-0.029	-0.008



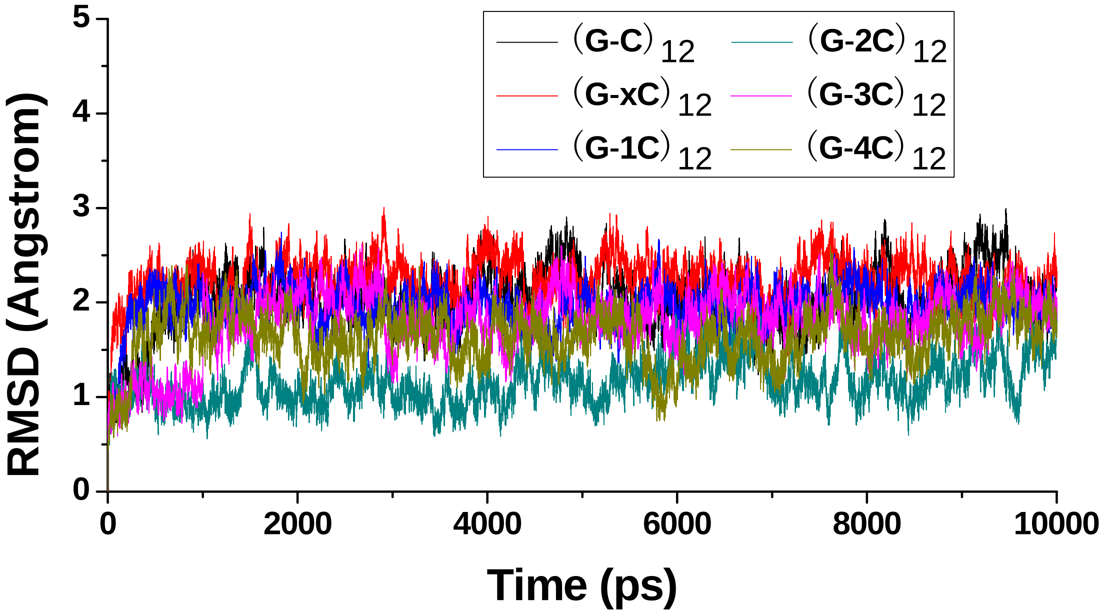
G-xC G-1C

G-2C G-3C G-4C

A-xT A-1T

A-2T A-3T A-4T

Figure S1. The optimized geometries of **G-nC** and **A-nT**.



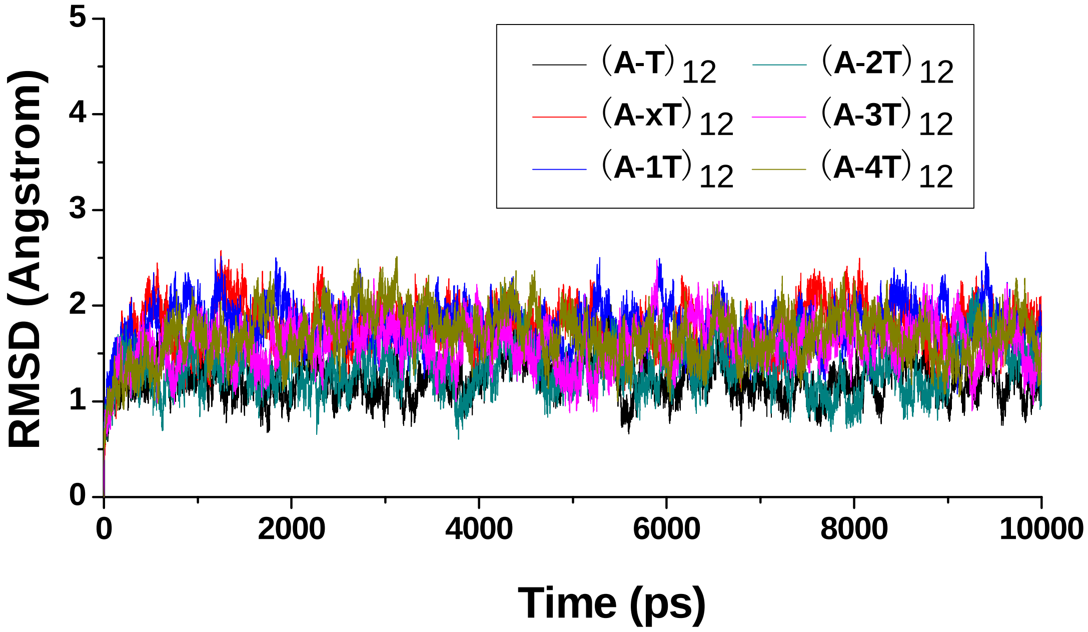


Figure S2. The all-atom root-mean-square deviations (RMSD) of the natural and the modified duplex helixes over the MD simulations. The centre eight base pairs are considered with respect to the starting conformations.

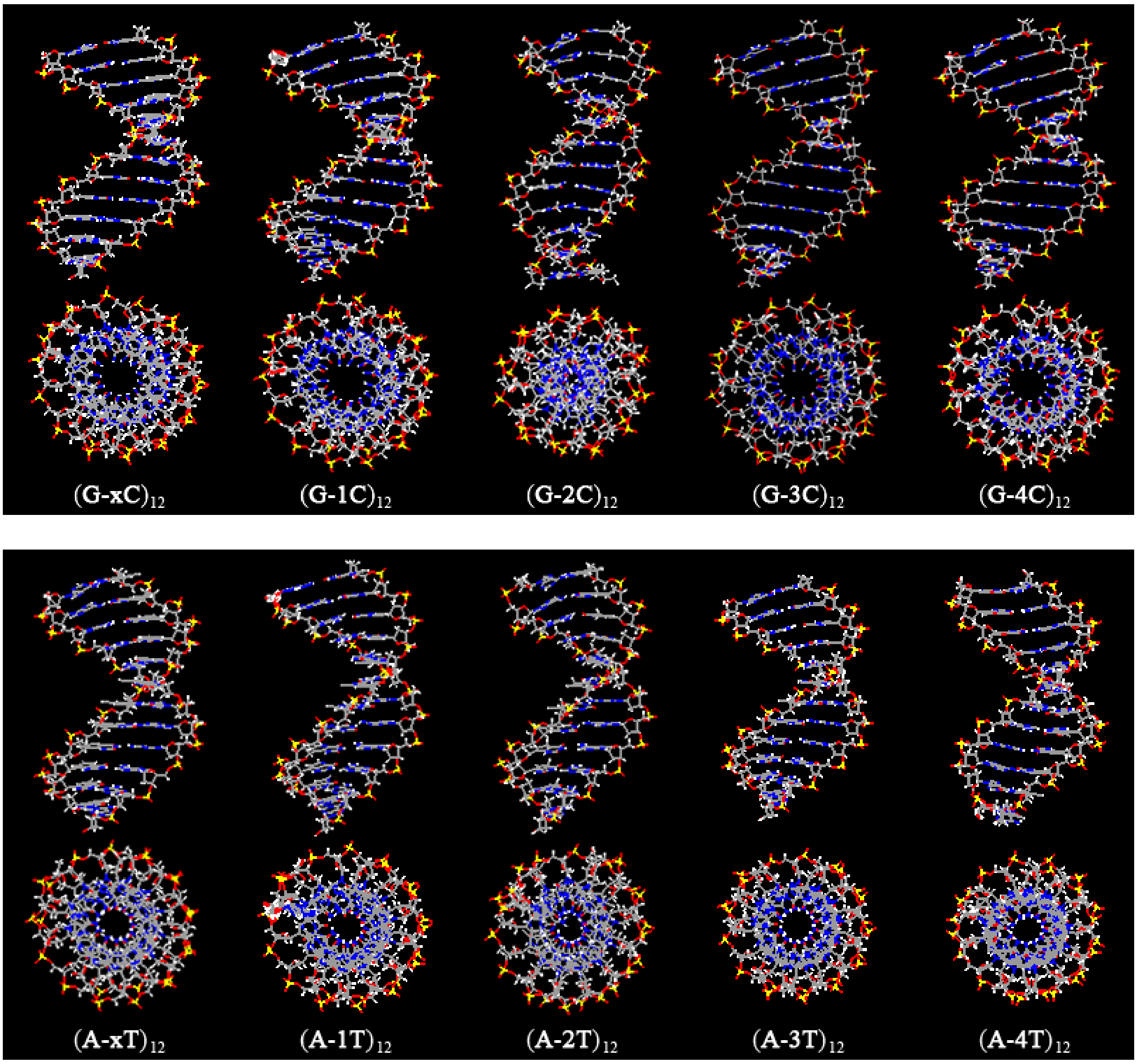


Figure S3. Average structures of (**nC·G**)$_{12}$ and (**nT·A**)$_{12}$, which are generated from the last 2 ns of MD simulations.

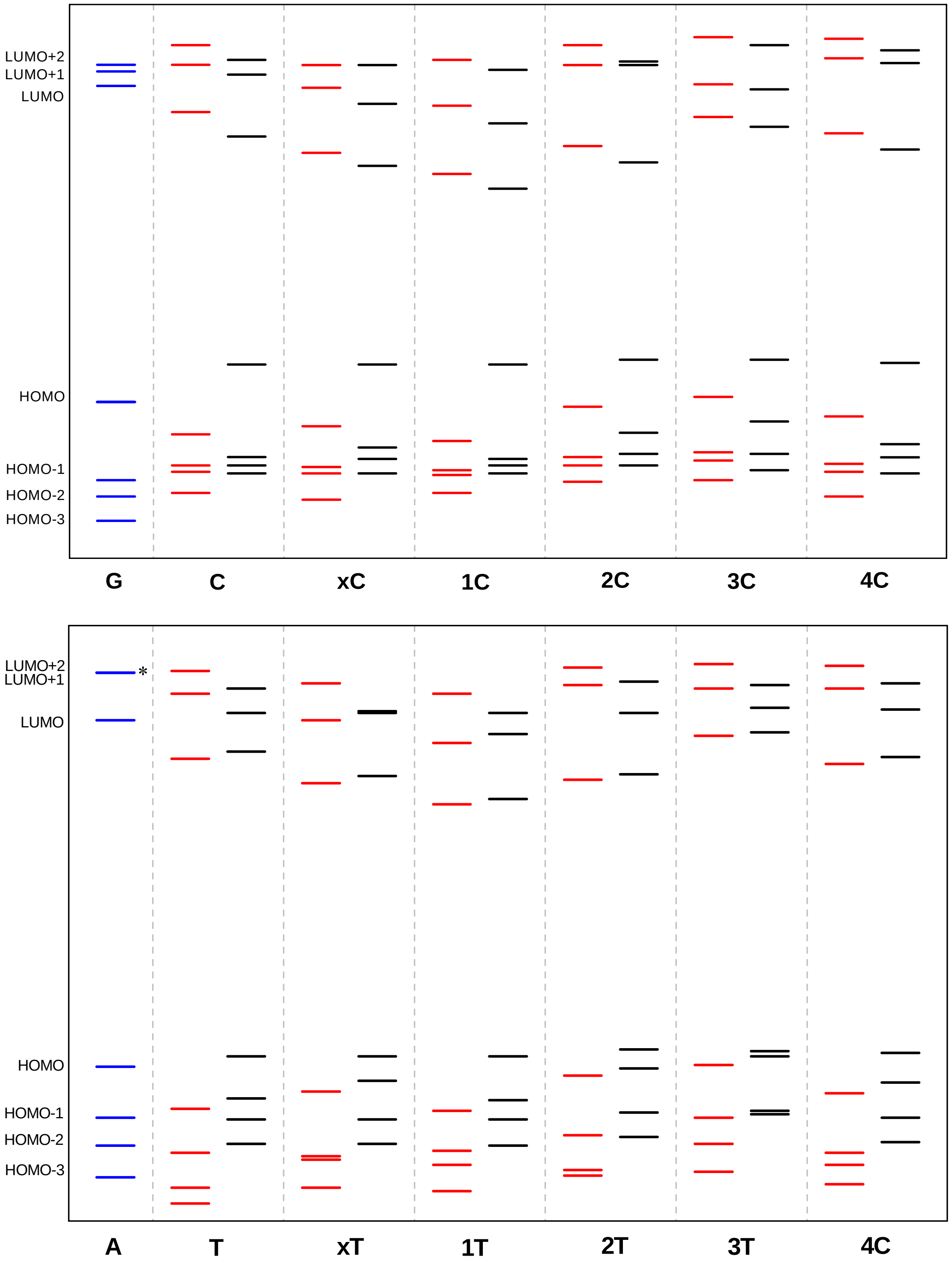
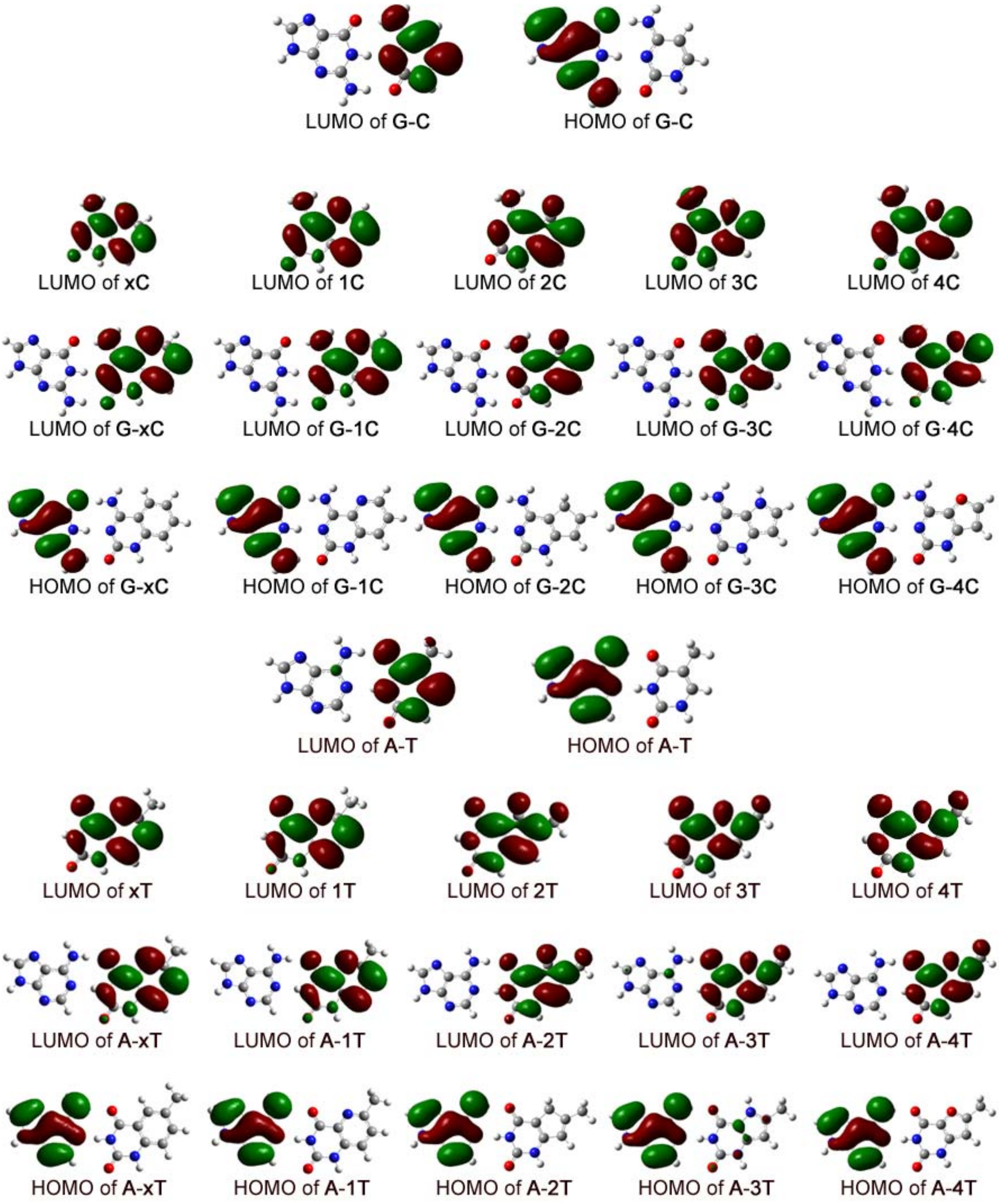


Figure S4. HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 of bases and base pairs. The first blue column refers to orbital energies of natural guanine and adenine. The red lines of each column refer to orbital energies of natural and size-expanded cytosine and thymine. The black lines refer to orbital energies of corresponding base pairs. Note. [*]These two energy levels are too close to distinguished.



LUMO of **G-C** HOMO of **G-C**

LUMO of **xC** LUMO of **1C** LUMO of **2C** LUMO of **3C** LUMO of **4C**

LUMO of **G-xC** LUMO of **G-1C** LUMO of **G-2C** LUMO of **G-3C** LUMO of **G·4C**

HOMO of **G-xC** HOMO of **G-1C** HOMO of **G-2C** HOMO of **G-3C** HOMO of **G-4C**

LUMO of **A-T** HOMO of **A-T**

LUMO of **xT** LUMO of **1T** LUMO of **2T** LUMO of **3T** LUMO of **4T**

LUMO of **A-xT** LUMO of **A-1T** LUMO of **A-2T** LUMO of **A-3T** LUMO of **A-4T**

HOMO of **A-xT** HOMO of **A-1T** HOMO of **A-2T** HOMO of **A-3T** HOMO of **A-4T**

Figure S5. Frontier molecular orbitals of the natural and the size-expanded bases and base pairs.

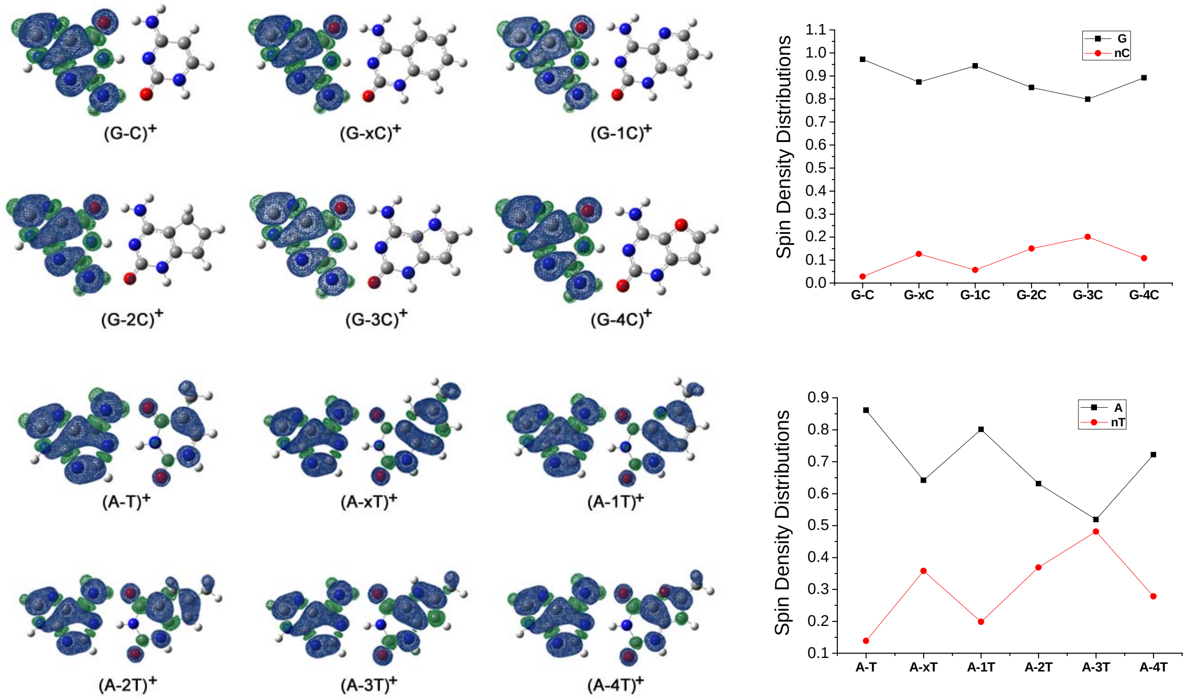
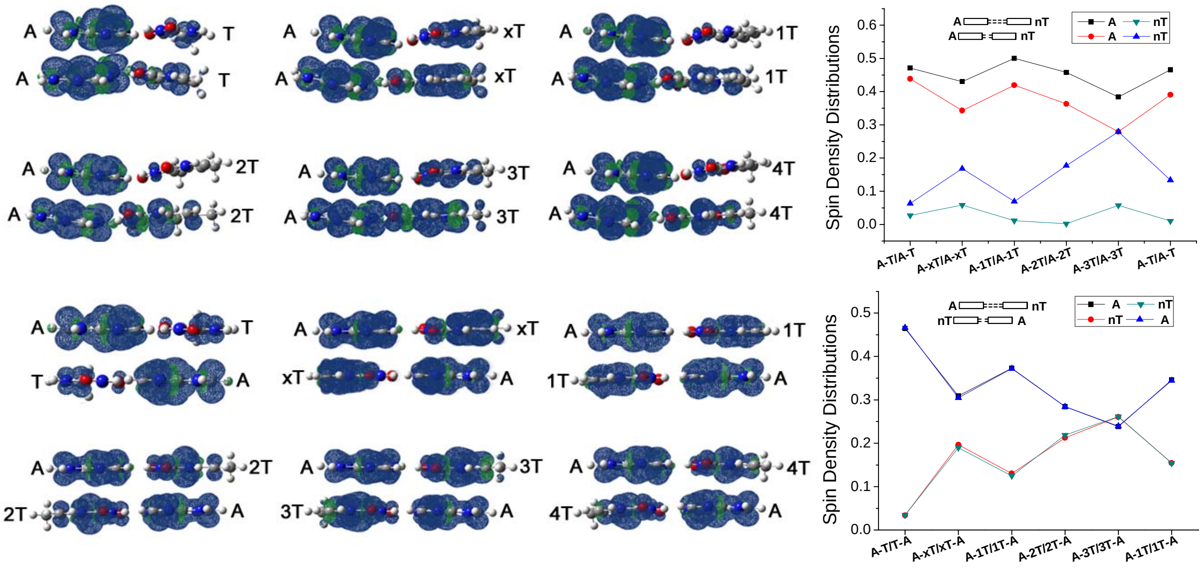


Figure S6. Spin density distributions of the oxidized natural and size-expanded **G-C** and **A-T** pairs.



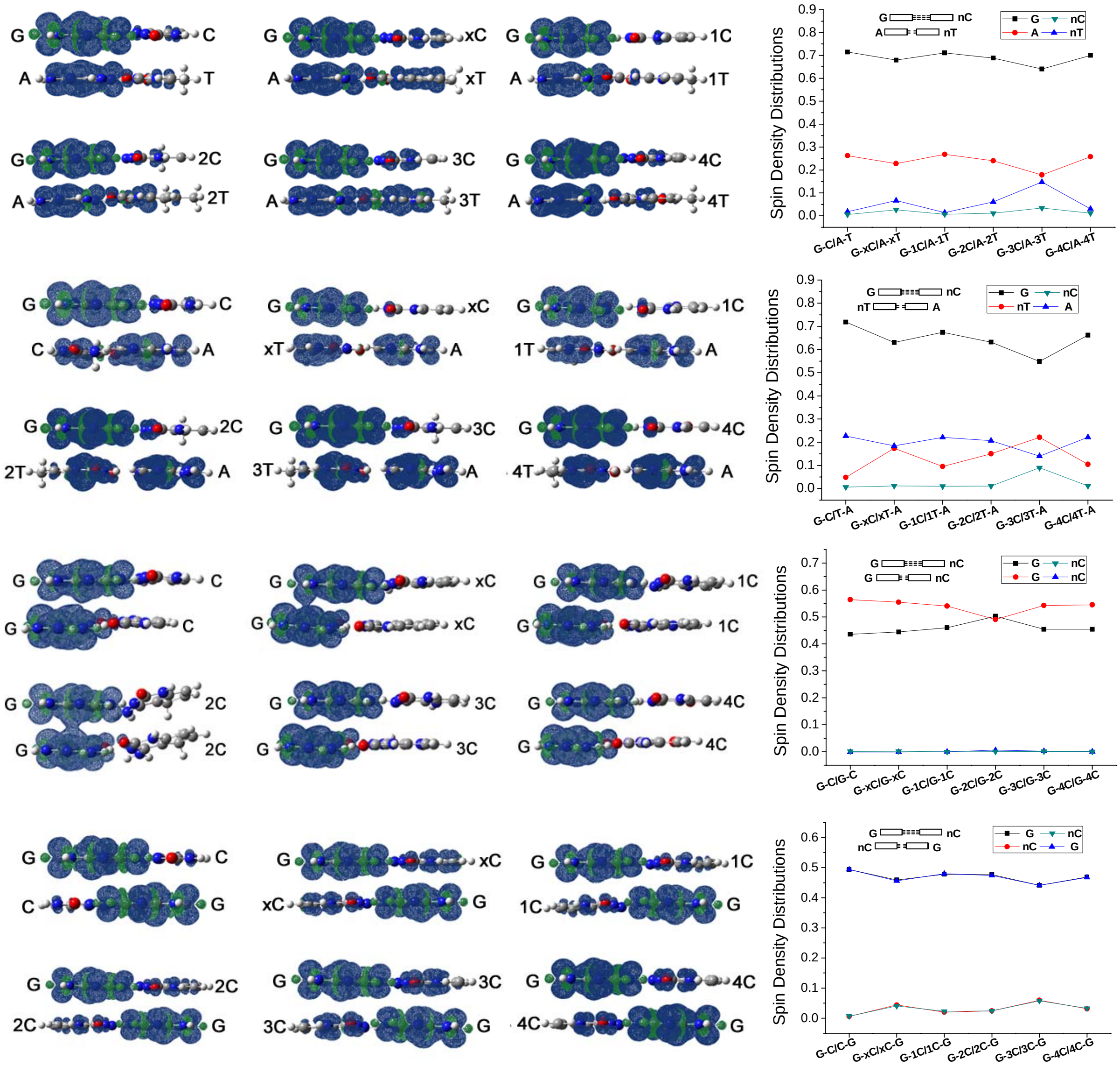
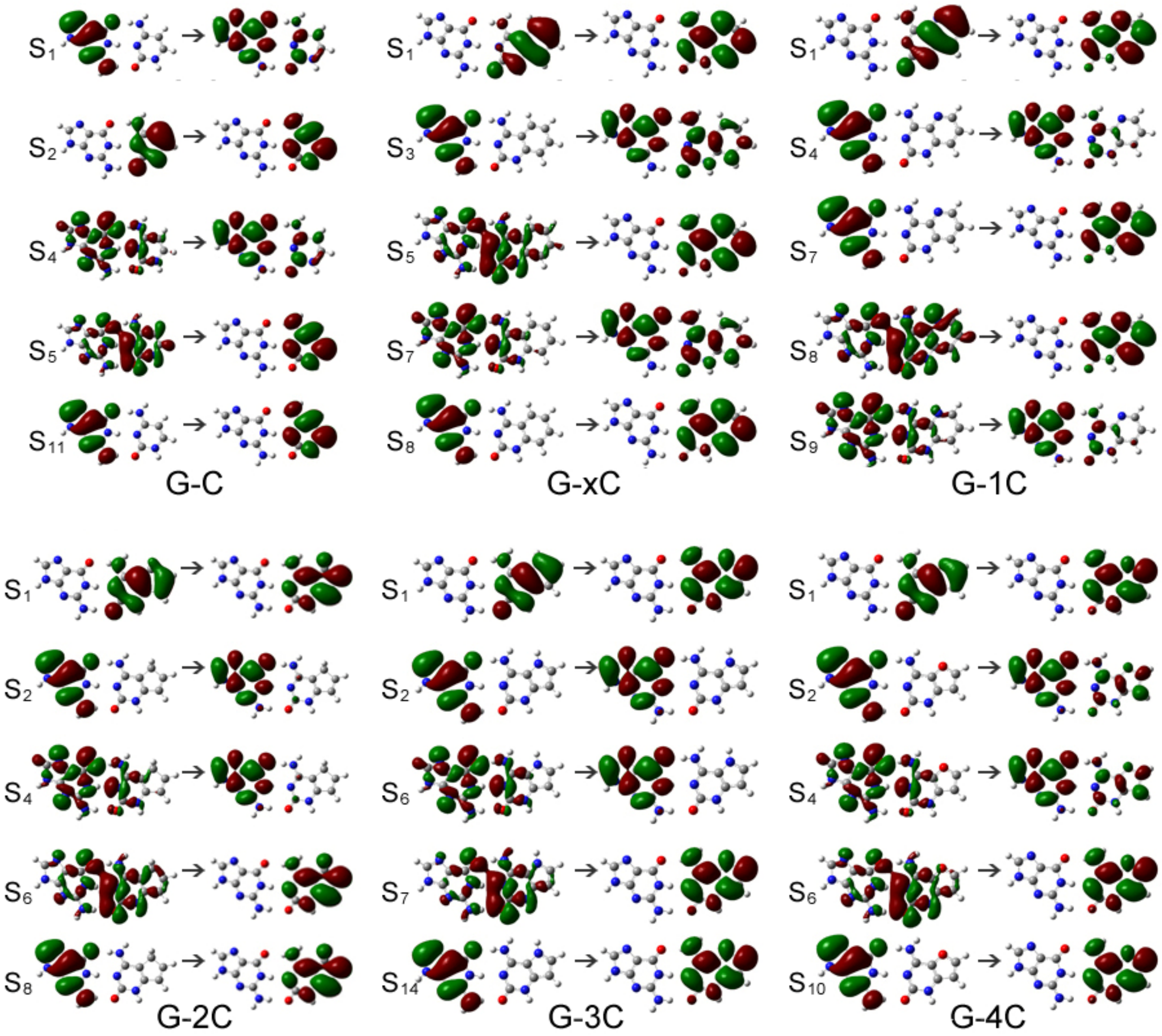


Figure S7. Spin density distribution of the oxidized natural and modified two-layer base pairs.


S_1
S_2
S_4
S_5
S_{11}
G-C
S_1
S_3
S_5
S_7
S_8
G-xC
S_1
S_4
S_7
S_8
S_9
G-1C
S_1
S_2
S_4
S_6
S_8
G-2C
S_1
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S_6
S_{10}
G-4C

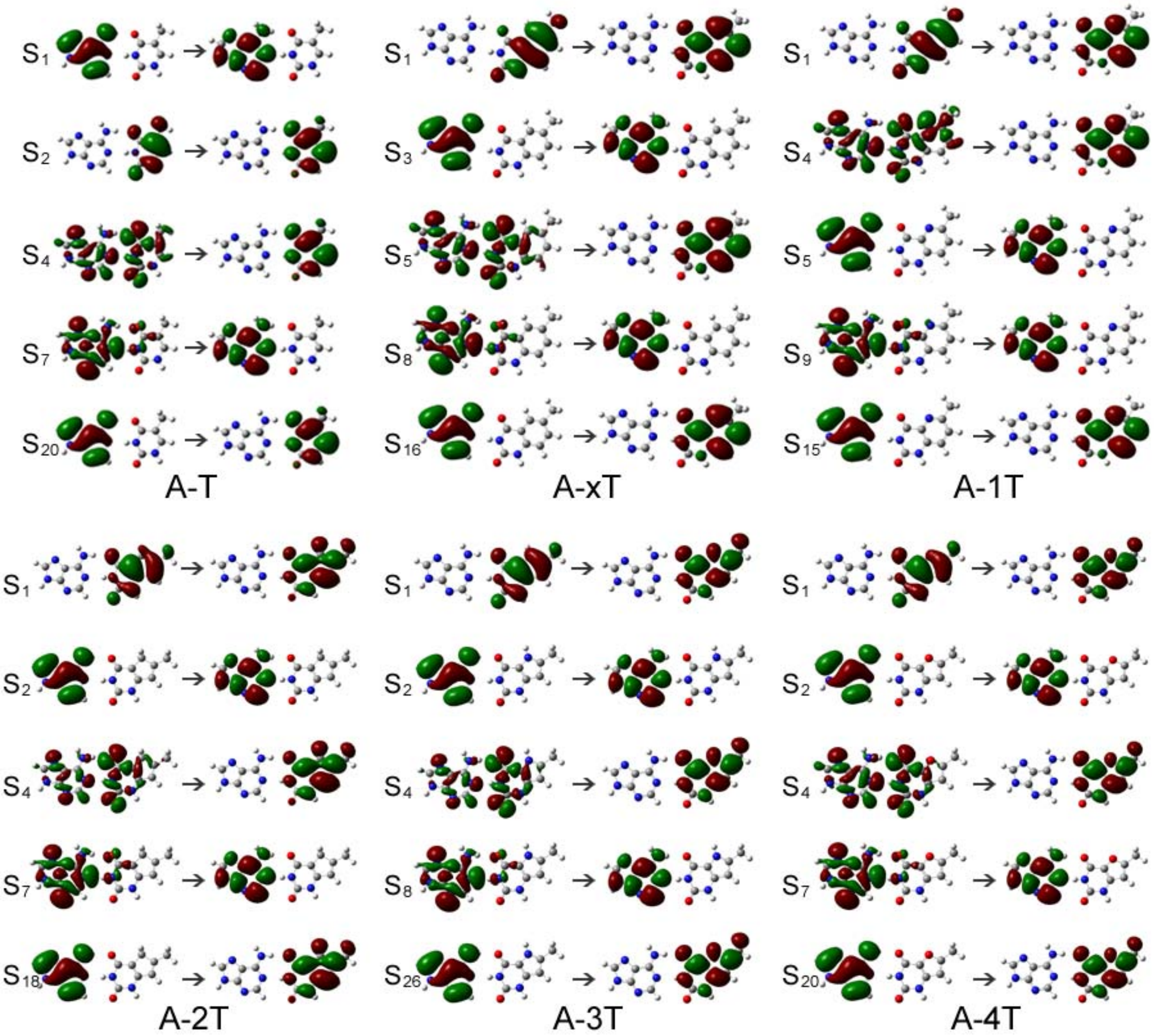
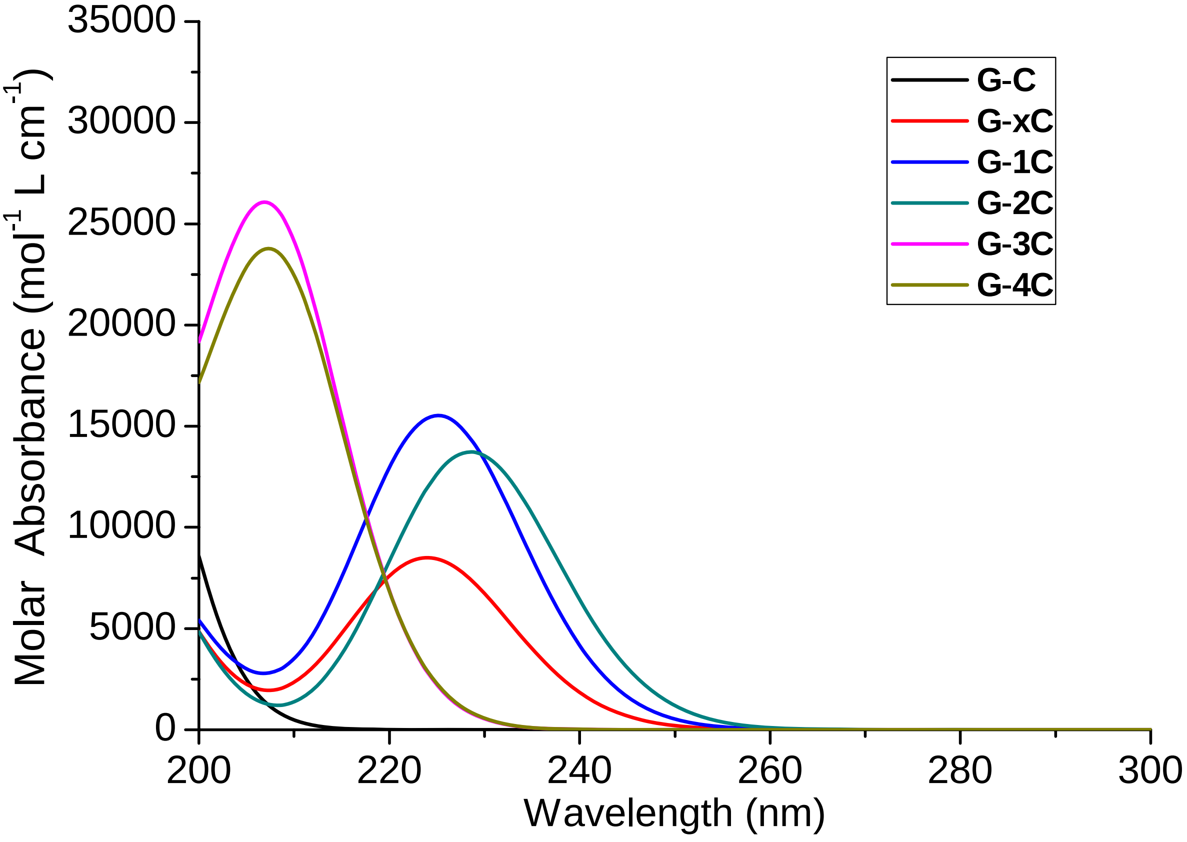


Figure S8. Molecular orbitals involved in several singlet transitions which were mentioned in Table S3.



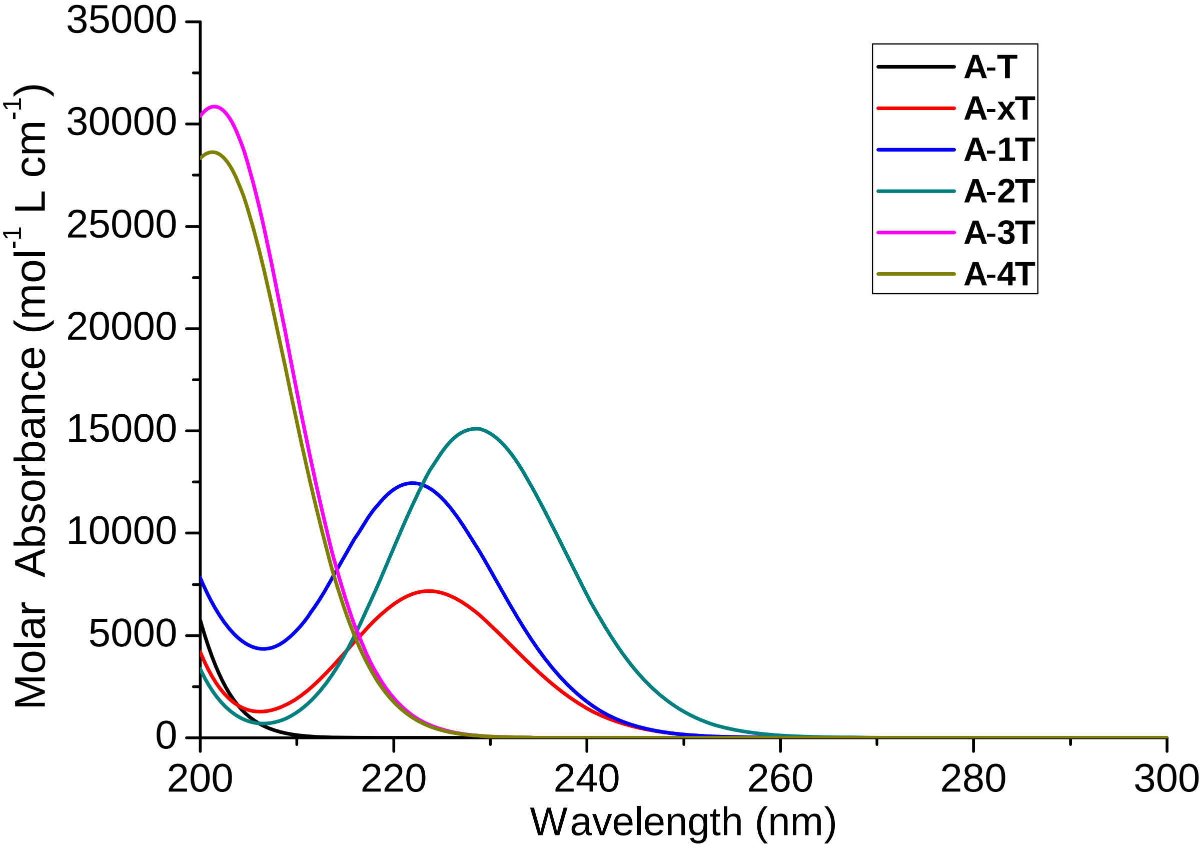


Figure S9. UV absorption spectra of the natural and the size-expanded **G-C** and **A-T** pairs.