Supporting Information of "Theoretical Studies on the Photophysics and Photochemistry of 5-Formylcytosine and 5-Carboxylcytosine: The Oxidative Products of Epigenetic Modification of Cytosine in DNA"

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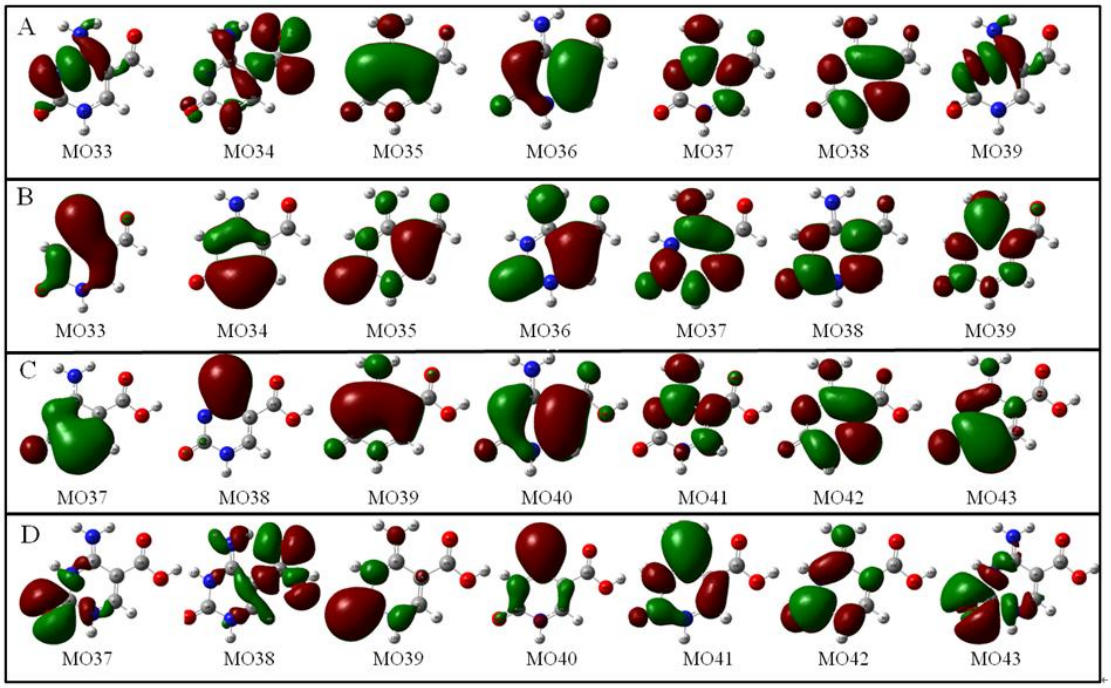

Figure S1. The active orbitals of 5fC and 5caC at CAS(8,7)/6-31G(d) level. A: 5fC-N, B: 5fC-P, C: 5caC-N and D: 5caC-P.

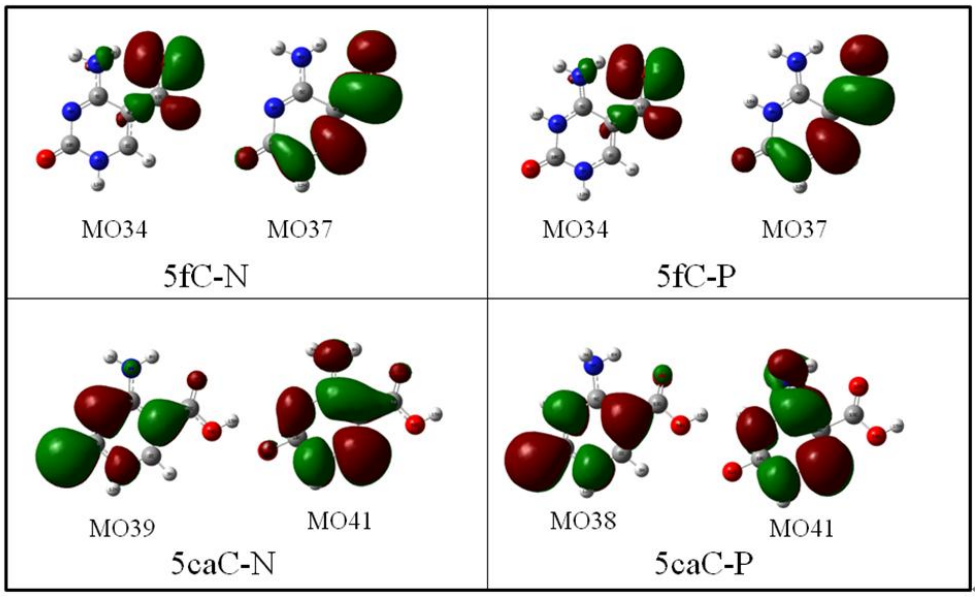

Figure S2. The transition molecular orbitals for S_1 states of 5fC and 5caC at CAS(8,7)/6-31G(d) level.

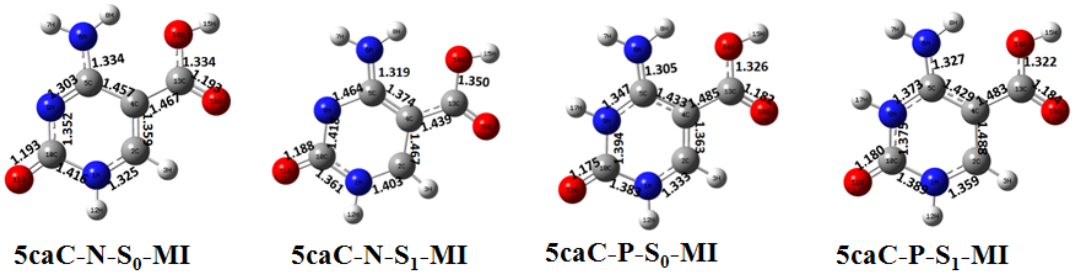

Figure S3. The structures of S_0 and S_1 states for intramolecular isomers of 5fC and 5caC at CAS(8,7)/6-31G(d) level. Bond lengths are in Å.

Table S1. The energies of S_0 and S_1 states of 5caC and the intramolecular heterogeneous states at CAS(8,7)/6-31G(d) level. Energies are in hartree.

	Neutral	**Protonated**
S_0	-580.3114074	-580.699423
S_1	-580.182135	-580.484875
S_0-MI	-580.240971	-580.6207141
S_1-MI	-580.1055007	-580.458269

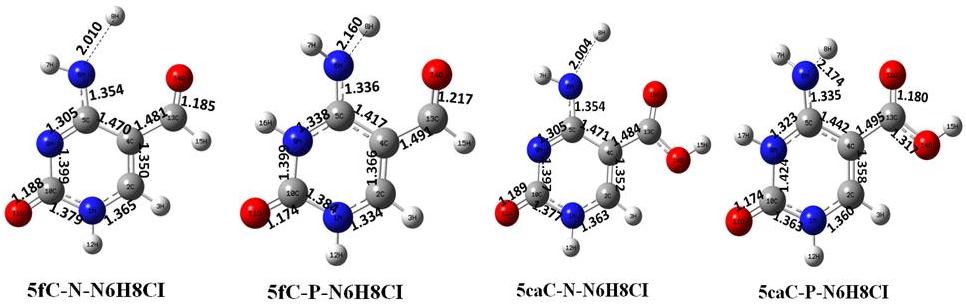

Figure S4. The optimized conical intersections of H8 atom dissociated from N6 of 5fC-N, 5fC-P, 5caC-N and 5caC-P. Bond lengths are in Å.

Table S2. The single point energies of the conical intersections for hydrogen transfer in triplet state of 5fC-N and 5fC-P at CASPT2//CAS(14,10)/6-31G(d) level. Energies are in kcal/mol.

Structure	Vacuum Relative Energy (kcal/mol)
5fC-N-N6H8CI	115.80
5fC-P-N6H8CI	118.47
5caC-N-N6H8CI	115.36
5caC-P-N6H8CI	138.76

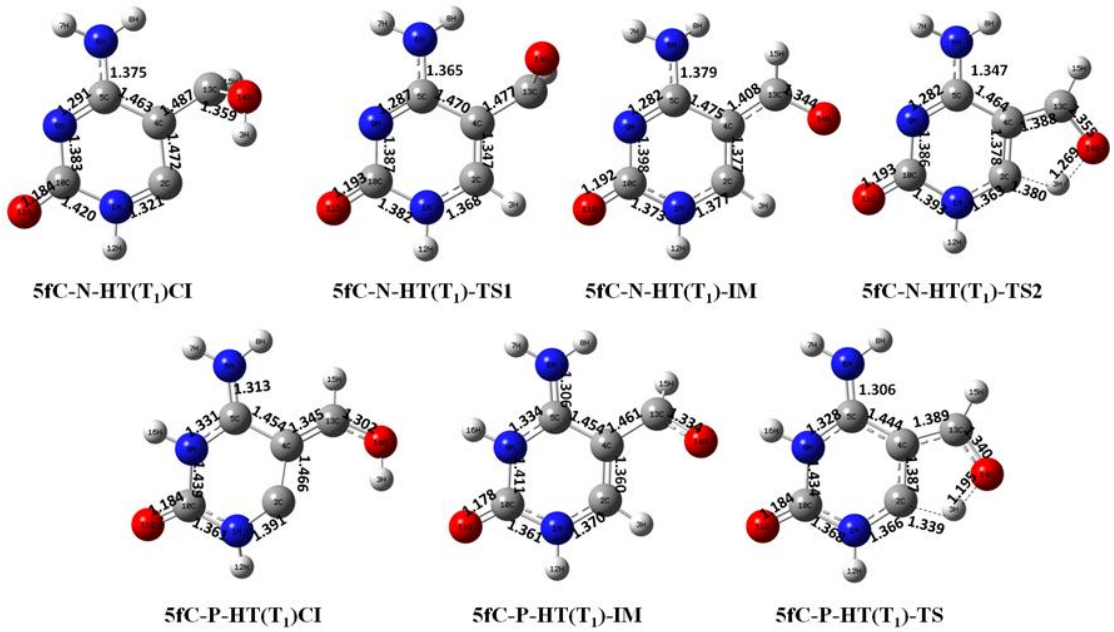

Figure S5. The optimized structures of the conical intersections, intermediates and transition states for hydrogen transfer in triplet state of 5fC-N and 5fC-P at CAS(8,7)/6-31G(d) level. Bond lengths are in Å.

Table S3. The single point energies of the conical intersections, intermediates and transition states for hydrogen transfer in triplet state of 5fC-N and 5fC-P at CASPT2//CAS(14,10)/6-31G(d) level and CASPT2//CAS(14,10)/6-31G(d)/PCM level for vacuum and PCM model, respectively. Energies are in kcal/mol.

Structure	Vacuum Relative Energy (kcal/mol)	PCM Relative Energy (kcal/mol)
5fC-N-HT(T_1)CI	118.33	114.26
5fC-N-HT(T_1)-TS1	92.91	81.77
5fC-N-HT(T_1)-IM	82.09	71.53
5fC-N-HT(T_1)-TS2	114.20	100.36
5fC-P-HT(T_1)CI	88.77	82.12
5fC-P-HT(T_1)-IM	78.03	72.35
5fC-P-HT(T_1)-TS	107.39	104.99