Supporting Information for:

Intramolecular Charge Transfer in 5-Halogen Cytidines Revealed by Femtosecond Time-resolved Spectroscopy

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Additional experimental and calculation results.

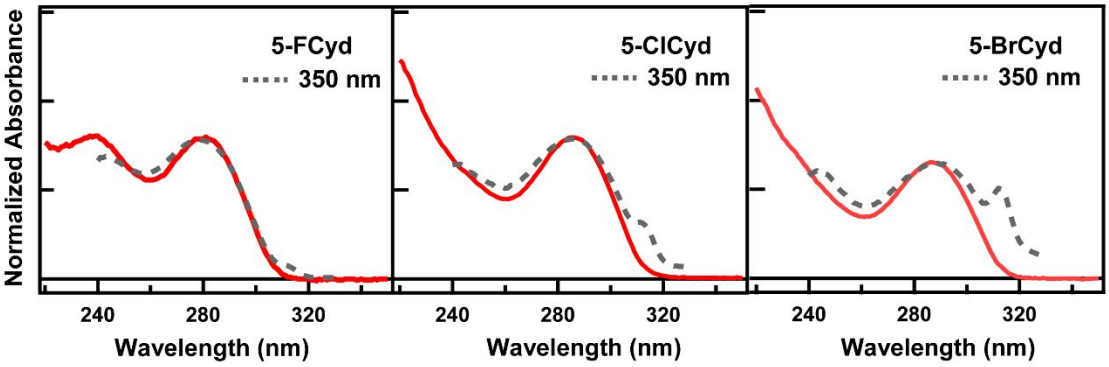

Figure S1. Steady-state absorption spectra (red line) and excitation spectra of 5-FCyd, 5-ClCyd and 5-BrCyd in buffer solution.

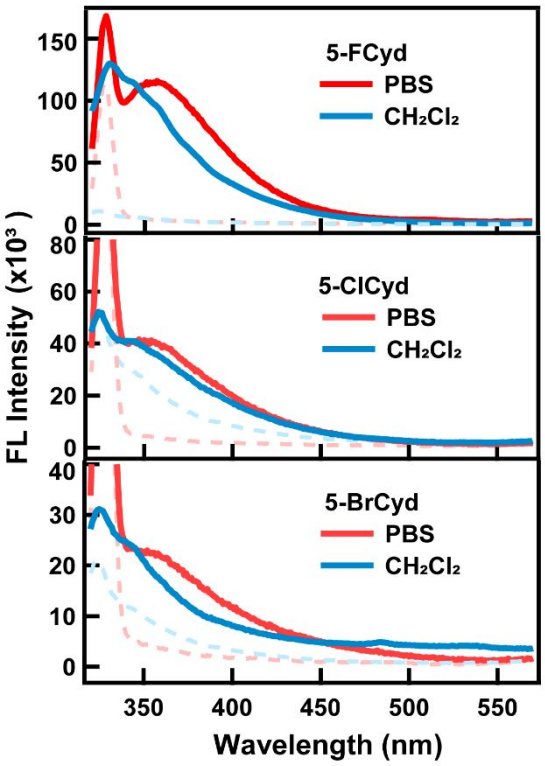

Figure S2. Fluorescence emission spectra of 5-FCyd, 5-ClCyd and 5-BrCyd in dichloromethane (compared with that in buffer solution). Signal strength is scaled for better comparison. Red and blue dash lines are background signal from pure solvent and cuvette.

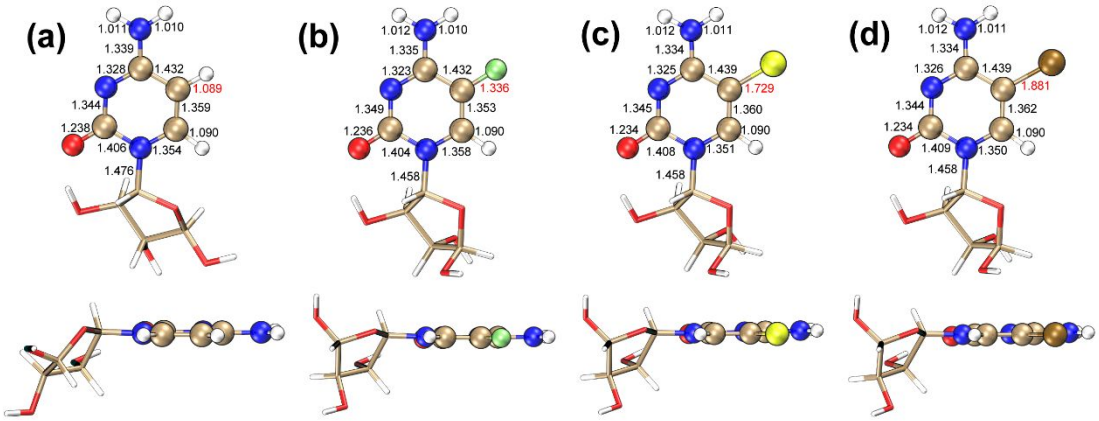

Figure S3. Equilibrium structures, S_0, of (a) Cyd, (b) 5-FCyd, (c) 5-ClCyd and (d) 5-BrCyd. Bond lengths are given in units of Å.

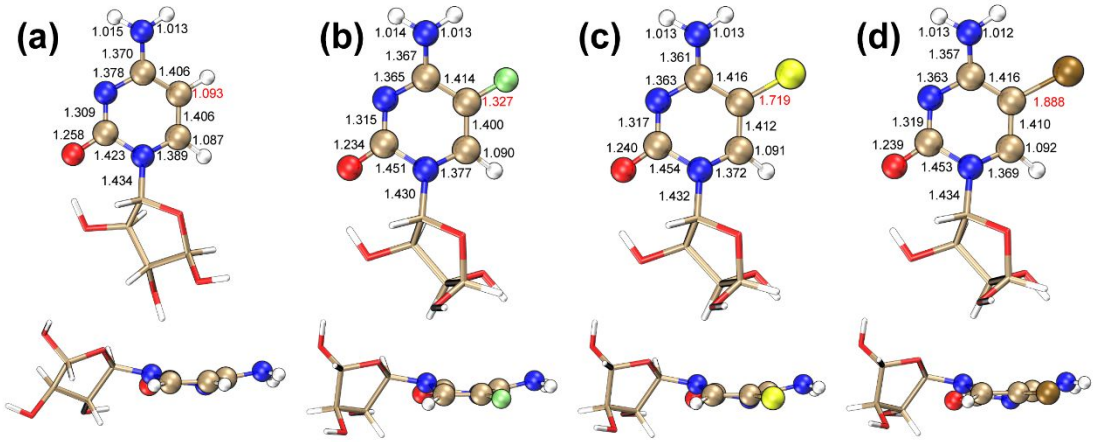

Figure S4. Minimum energy structures, (S_1)min, of (a) Cyd, (b) 5-FCyd, (c) 5-ClCyd and (d) 5-BrCyd. Bond lengths are given in units of Å.

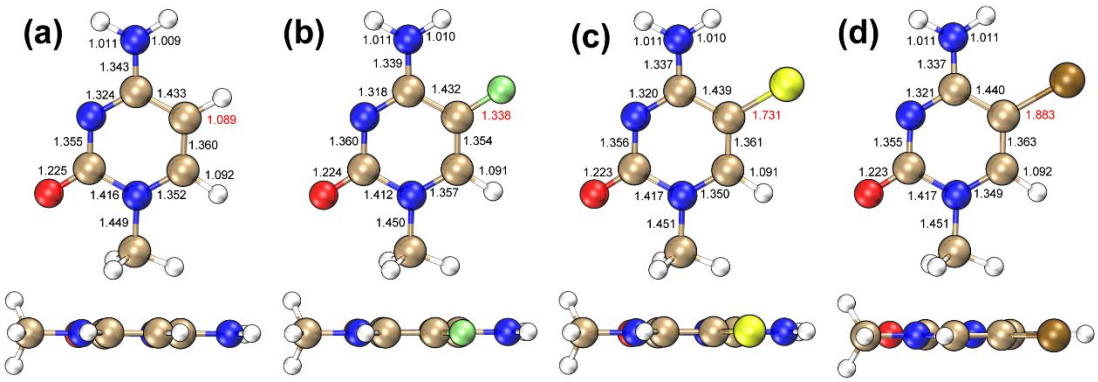

Figure S5. Equilibrium structures, S_0, of (a) MeCyt, (b) 5-FMeCyt, (c) 5-ClMeCyt and (d) 5-BrMeCyt. Bond lengths are given in units of Å.

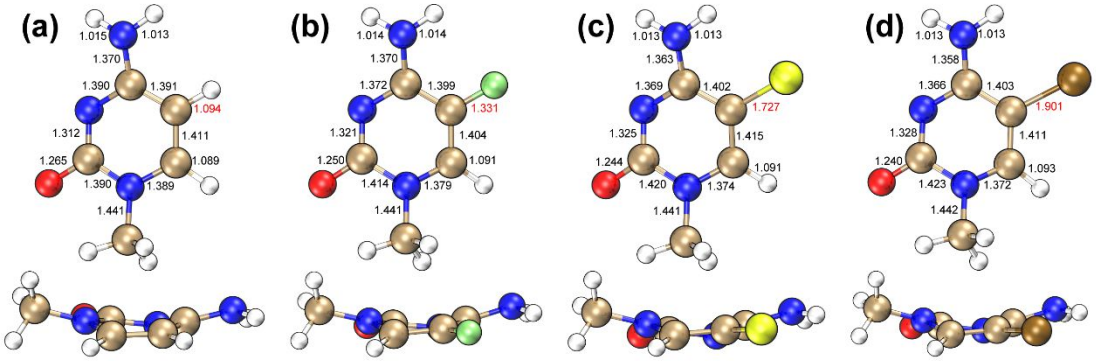

Figure S6. Minimum energy structures, (S_1)min, of (a) MeCyt, (b) 5-FMeCyt, (c) 5-ClMeCyt and (d) 5-BrMeCyt. Bond lengths are given in units of Å.

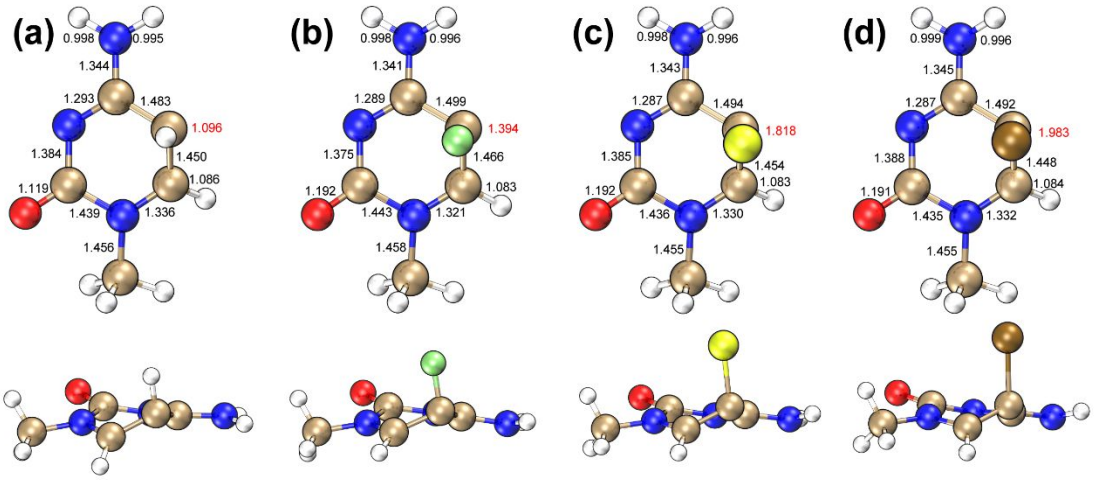

Figure S7. Conical intersection (CI) structures of (a) MeCyt, (b) 5-FMeCyt, (c) 5-ClMeCyt and (d) 5-BrMeCyt. Bond lengths are given in units of Å.

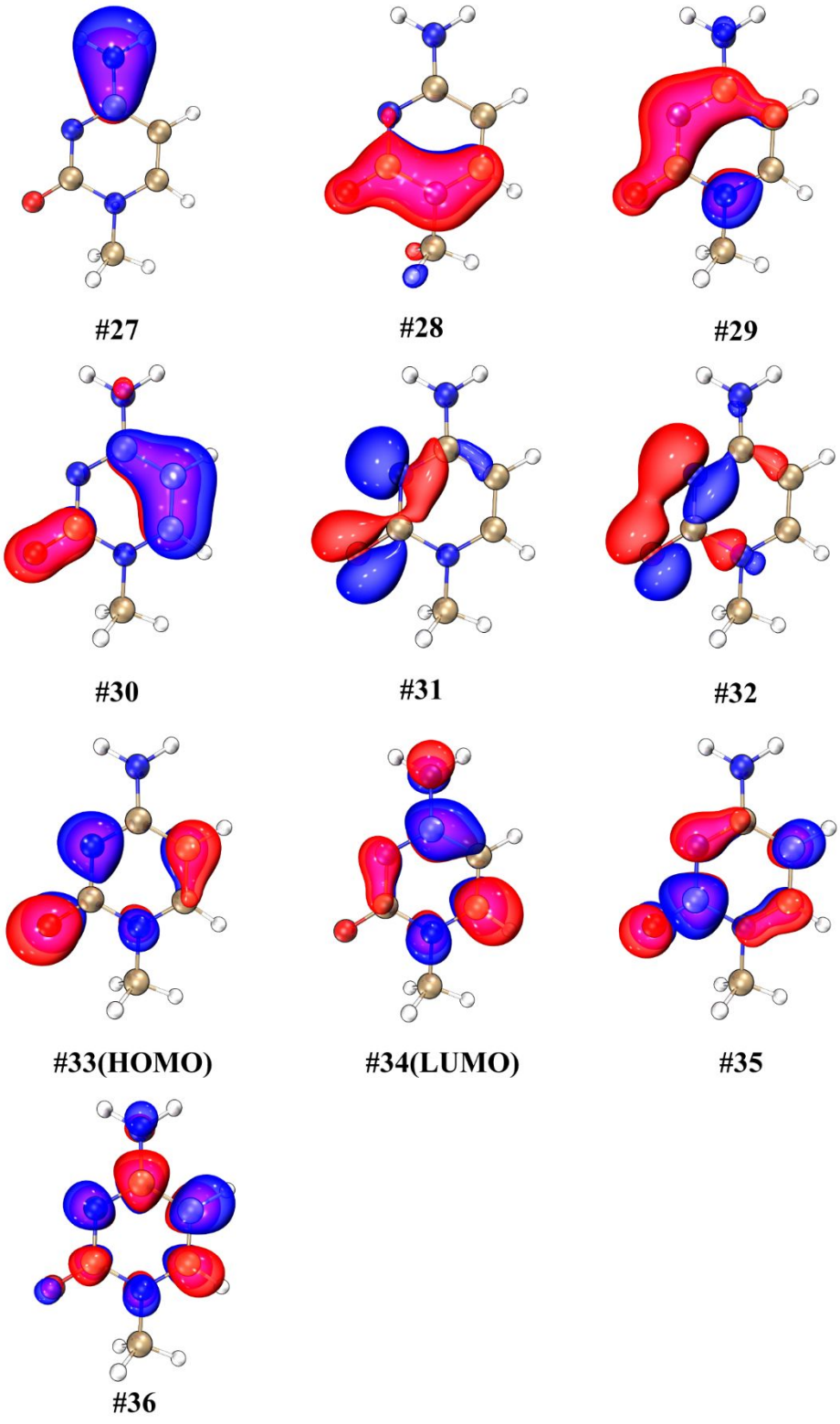

Figure S8. Active orbitals of MeCyt on the ground state in the SA(4)-CASSCF(14,10) calculation.

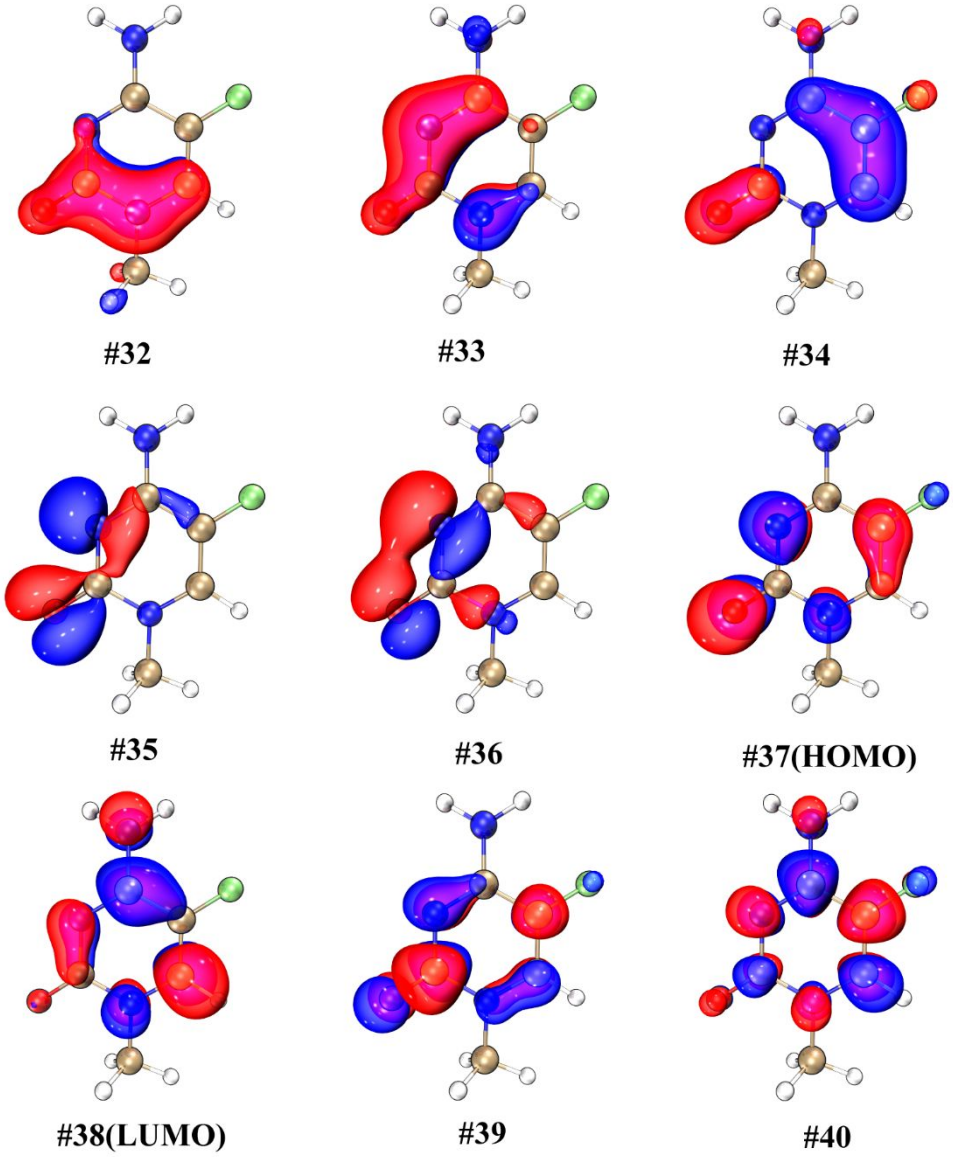

Figure S9. Active orbitals of 5-FMeCyt on the ground state in the SA(4)-CASSCF(12,9) calculation

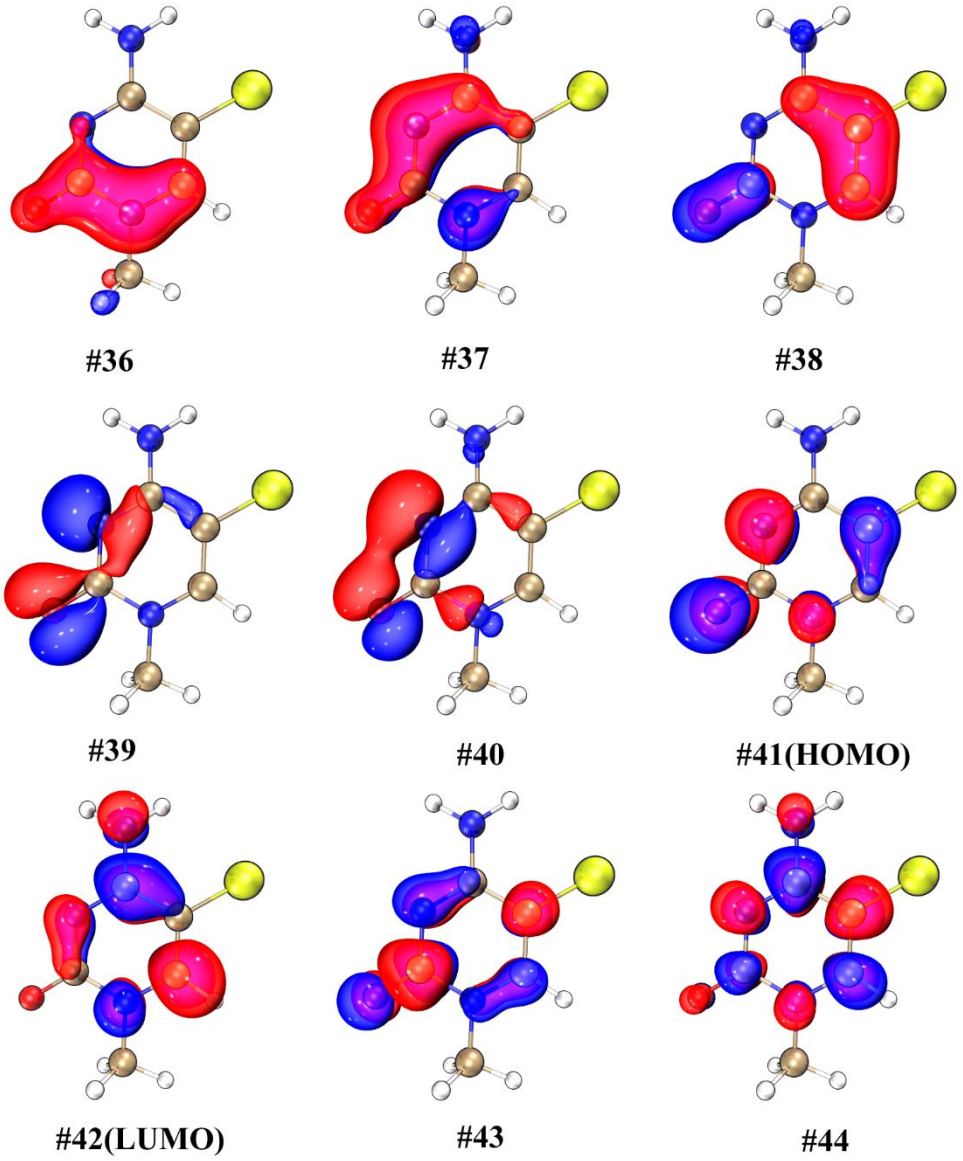

Figure S10. Active orbitals of 5-ClMeCyt on the ground state in the SA(4)-CASSCF(12,9) calculation.

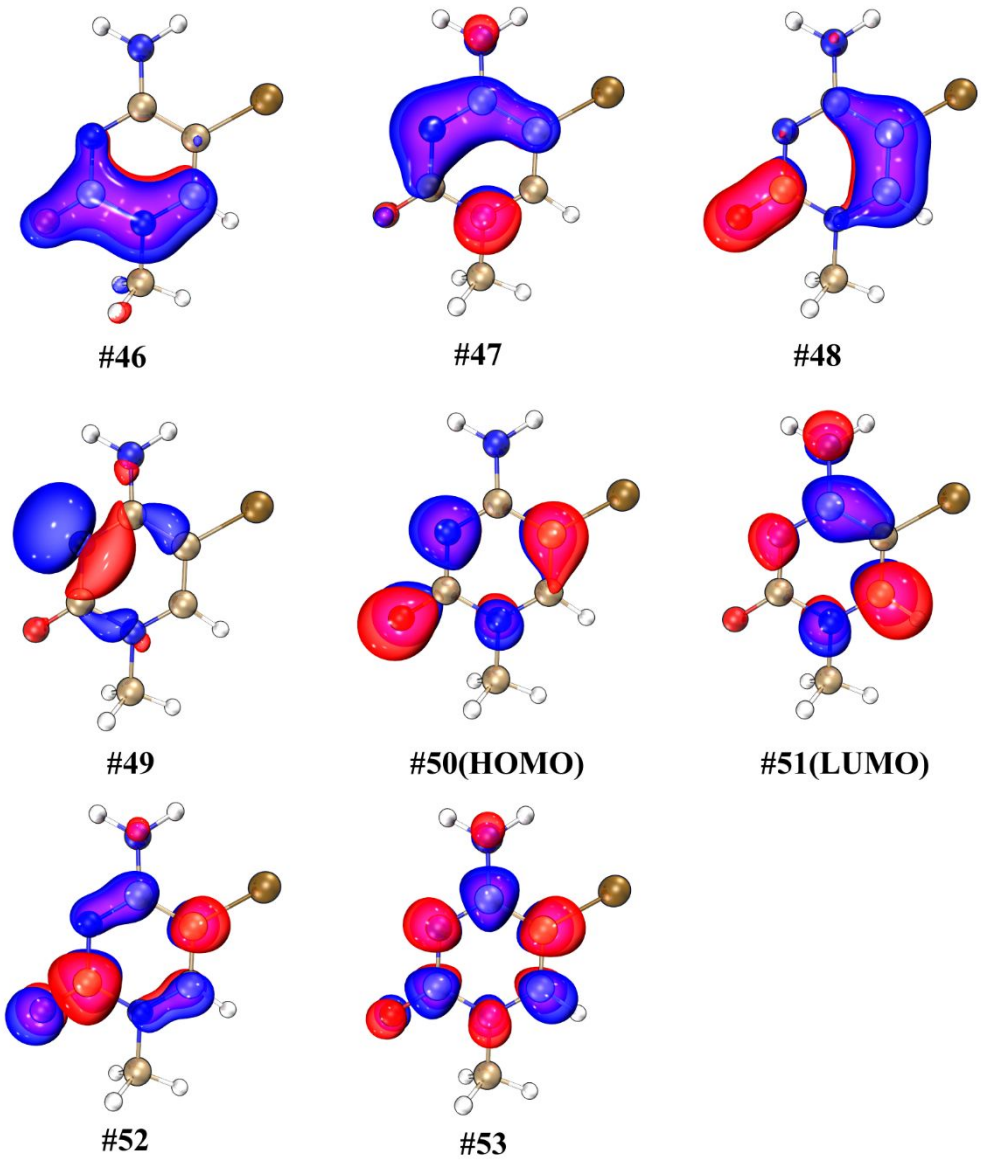

Figure S11. Active orbitals of 5-BrMeCyt on the ground state in the SA(3)-CASSCF(10,8) calculation.

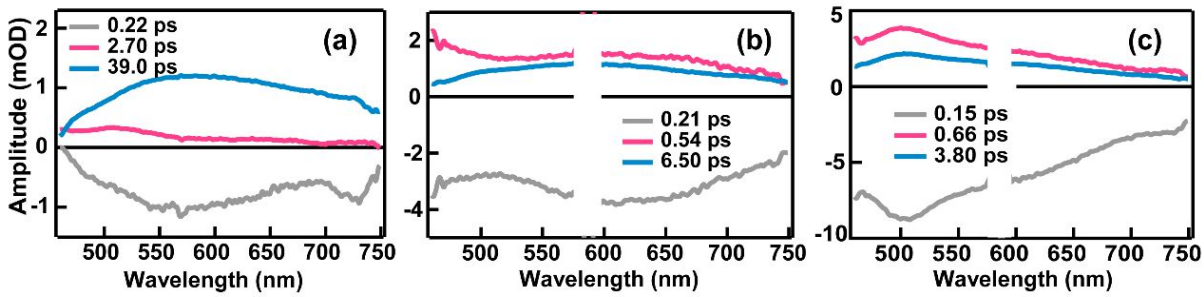

Figure S12. Decay associated spectra (DAS) of (a) 5-FCyd, (b) 5-ClCyd and (c) 5-BrCyd extracted from the global fitting.

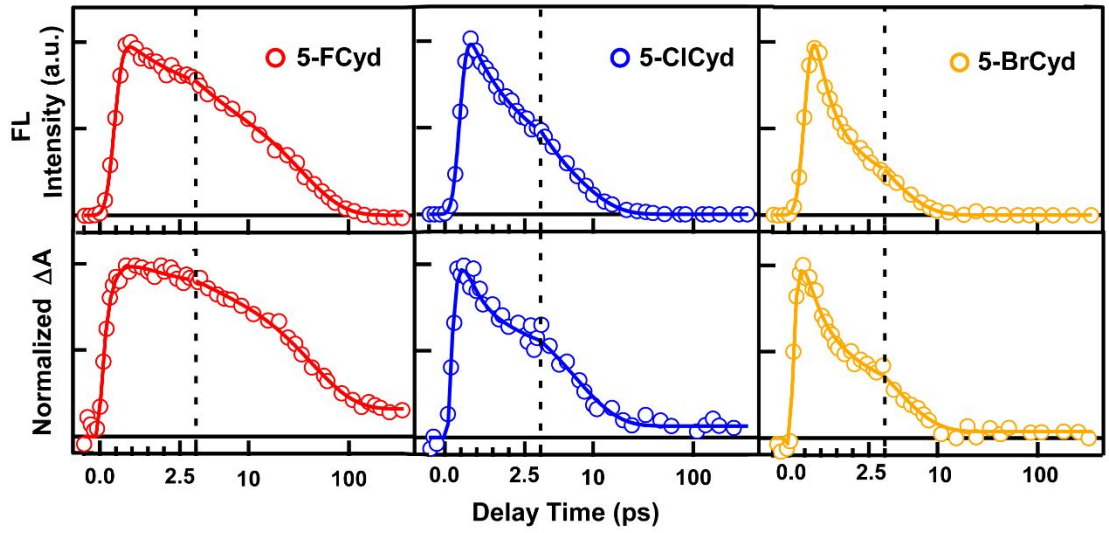

Figure S13. Comparison between fluorescence up-conversion kinetics at 350 nm (upper plane) and transient absorption kinetics at 680 nm (lower plane) of 5-FCyd, 5-ClCyd and 5-BrCyd in buffer solution with 295 nm excitation. Best-fitting parameters can be found in Table S8.

Table S1. Calculated vertical excitation energies (in eV) and oscillator strength (f) for lowest-lying singlet excited state (S_1) of 5-XCyd and 5-XMeCyt (X=H, F, Cl, Br) by (PCM)-TD-PBE0 method.

Mol	Gas	f	PCM	f	Exp. in water
Cyd	4.89	0.092	4.99	0.258	4.66
5-FCyd	4.68	0.123	4.73	0.277	4.42
5-ClCyd	4.66	0.117	4.69	0.261	4.34
5-BrCyd	4.64	0.113	4.66	0.252	4.34

Mol	Gas	f	PCM	f	Exp. in water
MeCyt	**4.79**	**0.058**	**4.94**	**0.203**	4.66
5-FMeCyt	**4.60**	**0.079**	**4.70**	**0.216**	4.42
5-ClMeCyt	**4.58**	**0.071**	**4.66**	**0.203**	4.34
5-BrMeCyt	**4.56**	**0.069**	**4.64**	**0.198**	4.34

Table S2. Calculated vertical emission energies (in eV) / fluorescence wavelength (in nm) and oscillator strength (f) for lowest-lying singlet excited state (S_1) of 5-XCyd and 5-XMeCyt (X=H, F, Cl, Br) by PCM(water)-TD-PBE0 method.

Mol	**Flu(eV/nm)**	**f**	**Mol**	**Flu(eV/nm)**	**f**	**Exp. in water(nm)**
Cyd	3.98(312)	0.164	**MeCyt**	**3.71(334)**	**0.068**	**323**
5-FCyd	3.57(347)	0.187	**5-FMeCyt**	**3.46(358)**	**0.112**	**354**
5-ClCyd	3.53(351)	0.172	**5-ClMeCyt**	**3.44(361)**	**0.106**	**352**
5-BrCyd	3.44(360)	0.152	**5-BrMeCyt**	**3.34(372)**	**0.094**	**350**

Table S3. The indexes of hole-electron analyses for lowest-lying singlet excited state (S_1) of 5-XCyd (X=H, F, Cl, Br) based on PCM(water)-TD-PBE0 calculation.

Mol	D(Å)	Sr	Hole (X%)	Electron (X%)	CT%/LE%	S_0-NPA(X)	S_1-NPA(X)	CT%/LE%
Cyd	1.28	0.64	0.2	0.6	0/100	0.260	0.250	1/99
5-FCyd	0.91	0.69	6	1	5/95	-0.345	-0.316	3/97
5-ClCyd	0.54	0.69	13	2	11/89	-0.002	0.077	8/92
5-BrCyd	0.48	0.70	17	6	11/89	0.082	0.158	8/92

D(Å) denotes the distance between centroids of hole and electron; Sr denotes the overlap between hole and electron (0<Sr<1); Hole% and Electron% represents the contribution of halogen atom on the hole and electron in the S_1 state. CT% is calculated by subtracting the Hole% with Electron% or the difference of NPA charges between ground state (S_0) and the first excited state (S_1).

Table S4. Calculated vertical excitation energies (in eV) for low-lying singlet excited States of 5-XMeCyt (X=H, F, Cl) calculated by SA(4)-CASSCF(12,9), SS-CASPT2 and MS(4)-CASPT2(12,9). The results for MeCyt by SA(4)-CASSCF(14,10), SS-CASPT2 and MS(4)-CASPT2(14,10) are also listed.

Mol		SA-CASSCF			SS-CASPT2	MS-CASPT2	Exp.
		Characteristic	ΔE/eV	f	ΔE/eV	ΔE/eV	
MeCyt	S1	ππ*	4.91	0.0698	4.26	**4.55**	**4.66**
(14,10)	S2	nπ*	5.20	0.0001	5.01	4.98	
MeCyt	S1	ππ*	4.91	0.0778	4.23	**4.53**	**4.66**
(12,9)	S2	nπ*	5.17	0.0002	4.98	4.95	
5-FMeCyt	S1	ππ*	4.91	0.0822	4.14	**4.42**	**4.42**
(12,9)	S2	nπ*	5.09	0.0001	5.03	5.06	
5-ClMeCyt	S1	ππ*	4.84	0.0706	4.11	**4.41**	**4.34**
(12,9)	S2	nπ*	5.12	0.0000	4.93	4.61	

Table S5. Calculated vertical excitation energies (in eV) for low-lying singlet excited States of 5-XMeCyt (X=H, F, Cl, Br) calculated by SA(3)-CASSCF(10,8), SS-CASPT2 and MS(3)-CASPT2(10,8).

Mol		SA-CASSCF			SS-CASPT2	MS-CASPT2	Exp.
		Characteristic	ΔE/eV	f	ΔE/eV	ΔE/eV	
MeCyt	S_1	ππ*	4.77	0.0737	4.28	**4.48**	**4.66**
	S_2	nπ*	5.07	0.0003	5.22	5.33	
5-FMeCyt	S_1	ππ*	4.75	0.0766	4.18	**4.38**	**4.42**
	S_2	nπ*	4.95	0.0003	5.09	5.19	
5-ClMeCyt	S_1	ππ*	4.69	0.0736	4.16	**4.36**	**4.34**
	S_2	nπ*	5.01	0.0034	5.14	5.24	
5-BrMeCyt	S_1	ππ*	5.00	0.0717	4.09	**4.34**	**4.34**
	S_2	nπ*	5.10	0.0003	4.98	5.10	

Table S6. Adiabatic Excitation Energies (in eV) for the lowest $^1\pi\pi^*$ states of 5-XMeCyt (X=H, F, Cl, Br) calculated by MS-CASPT2 on various levels.

Mol	MS(4)-CASPT2(14,10)	MS(4)-CASPT2(12,9)	MS(3)-CASPT2(10,8)	MS(2)-CASPT2(8,7)	Exp.[a]
MeCyt	3.95	3.92	3.95	3.97	3.96[b]
5-FMeCyt	-	3.77	3.78	3.80	3.80[c]
5-ClMeCyt	-	3.80	3.79	3.93	-
5-BrMeCyt	-	-	3.82	3.78	-

[a]Experimental values are given as the positions of the 0-0 band origin. [b]From ref 19 in the main text. [c]the value of 5-FCyt from ref 1 in SI.

Table S7. The potential energies (in eV) for the $^1\pi\pi^*$ state at $(^1\pi\pi^*)_{min}$ and ethene-like CI ($^1\pi\pi^*$/gs) structure of 5-XMeCyt (X=H, F, Cl, Br) calculated at the MS(2)-CASPT2(8,7) level.

Mol	$(^1\pi\pi^*)_{min}$	$(^1\pi\pi^*/gs)_{CI}$	ΔE
MeCyt	3.97	3.74	-0.23
5-FMeCyt	3.80	3.43	-0.37
5-ClMeCyt	3.93	3.86	-0.07
5-BrMeCyt	3.78	3.74	-0.04

Table S8. Best fitting parameters of TA at 680 nm for 5-FCyd, 5-ClCyd and 5-BrCyd.

	τ_1 (ps)	A_1 %	τ_2 (ps)	A_2 %	τ_3 (ps)	A_3 %	A_4 %
5-FCyd	0.22 ± 0.10	-52	2.7 ± 1.2	6	39 ± 1	34	8
5-ClCyd	0.21 ± 0.10	-52	0.54 ± 0.31	25	6.5 ± 0.6	20	3
5-BrCyd	0.15 ± 0.10	-54	0.66 ± 0.14	25	3.8 ± 0.3	18	3

Reference

1. Lobsiger, S.; Trachsel, M. A.; Den, T.; Leutwyler, S. Excited-state structure, vibrations, and nonradiative relaxation of jet-cooled 5-fluorocytosine. *J. Phys. Chem. B* **2014**, *118*, 2973-2984.