Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

UV/Vis absorption and SS emission spectra of 8N2OH

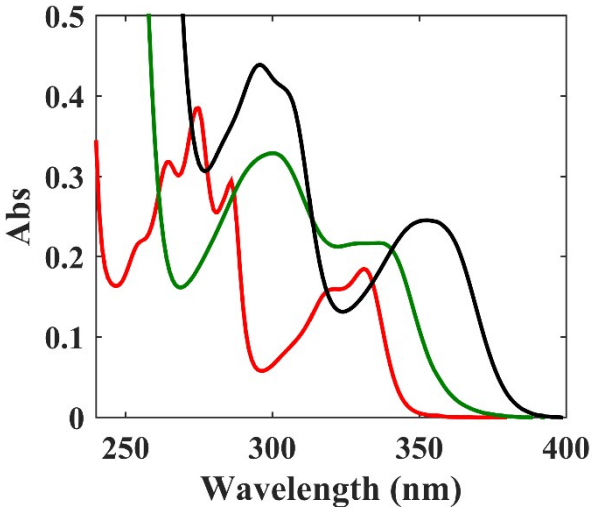


Figure SI_1. UV/Vis spectra of the different protonation states of 8N2OH in the ground state: cation (pH = 2.2, red), neutral, (pH = 7.7, green), and anion (pH = 11.2, black). $pK_{a1}(NH_3^+/NH_2)$ and $pK_{a2}(OH/O^-)$ were determined to be 4.2 ± 0.2 and 9.5 ± 0.2, respectively.

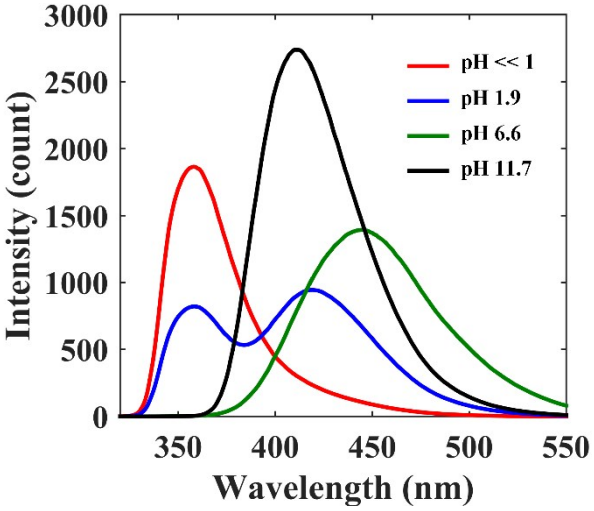


Figure SI_2. Steady-state emission spectra of the different protonation states of 8N2OH in the excited state: in the low pH regime, the predominant cation (pH <<1, red) and combination of cation and zwitterion (pH = 1.9, blue), in the mid pH regime, neutral (pH = 6.6, green), and in the high pH regime, the anion (pH = 11.7, black). The relative intensities fluctuated as described in the methodology section, but the peak positions and contours were similar to those observed for 5N2OH.

Table SI_1. Experimental and calculated S_1-S_0 absorption and emission transitions (nm) of the various protonation states of 8N2OH and 2OH.

Absorption	**8N2OH$_{expt}$**	**8N2OH$_{calc}$**	**2OH$_{expt}$**	**2OH$_{calc}$**
Cation	331	305	--	--
Zwitterion	-	348	--	--
Neutral	336	341	328	303
Anion	353	350	346	344

Emission	**8N2OH$_{expt}$**	**8N2OH$_{calc}$**	**2OH$_{expt}$**	**2OH$_{calc}$**
Cation	358	352	--	--
Zwitterion	422	423	--	--
Neutral	445	495	351	346
Anion	410	408	414	421

Kinetic modeling: fitting parameters of 5N2OH

Table SI_2 Lifetime parameters (τ) of 5N2OH data set determined at each pH from global fitting of TCSPC data collected at select wavelengths in the 350 nm – 525 nm range. The shaded region of the table was used for the excited cation-zwitterion equilibrium state model.

pH	**τ_1 (s)**	**τ_2 (s)**	**τ_3 (s)**	**τ_4 (s)**
0.6	1.82e-10	4.79e-9		
1.0	2.61e-10	5.72e-9		
1.6	5.03e-10	8.15e-9		
1.9	5.64e-10	9.73e-9		
4.0	6.24e-10	1.20e-8	2.01e-8	
6.7			2.11e-8	
9.4			2.11e-8	9.01e-9
11.3				9.01e-9

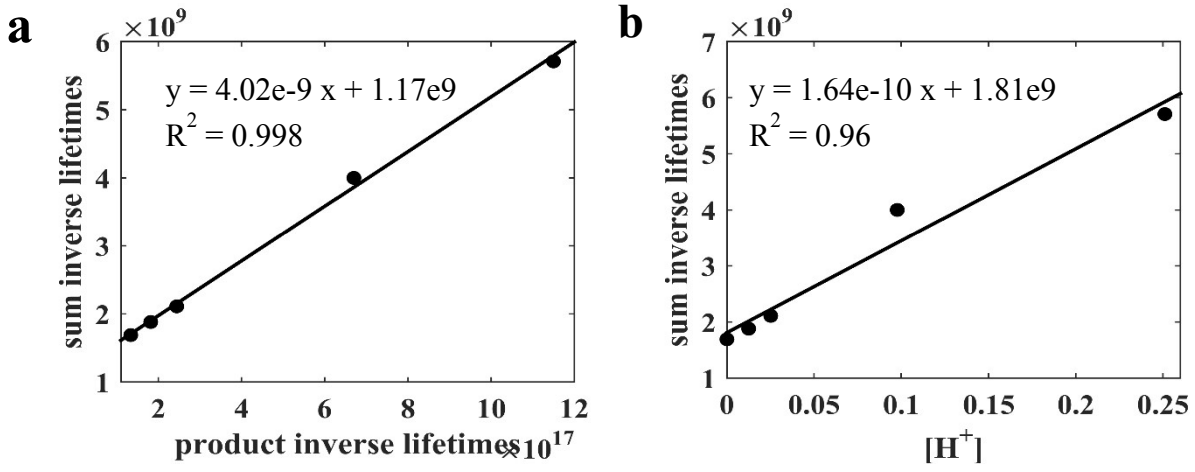


Figure SI_3. Linear plot analysis of the lifetimes from Table SI 2 to provide preliminary estimates of the k_A and k_a parameters (a) sum of inverse lifetimes ($\tau_1^{-1} + \tau_2^{-1}$) vs. product of inverse lifetimes ($\tau_1^{-1}\,\tau_2^{-1}$) where slope = k_A^{-1}); (b) sum of inverse lifetimes ($\tau_1^{-1} + \tau_2^{-1}$) vs. concentration of H^+ where slope = k_r

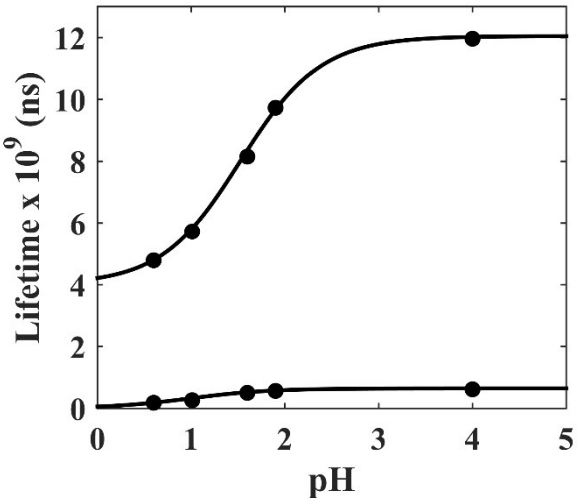


Figure SI_4. Lifetime vs. pH curves generated from fitting lifetime parameters (τ_1, τ_2) of 5N2OH from Table SI 2 to equation 3. The following kinetic parameters were obtained: k_A = 2.5e8, k_B = 8.3e7, k_r = 1.6e10, and k_d = 1.3e9 (pK_a^* = 1.1).

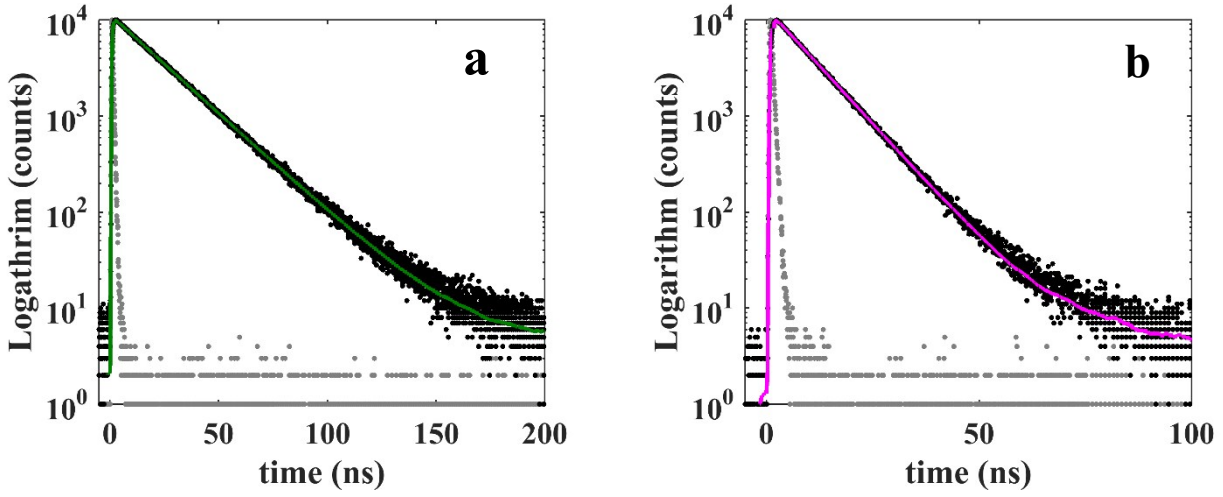


Figure SI_5. Select single wavelength emission decay at 450 nm (neutral) and 425-nm (anion) from TRES collected for 5N2OH (gray markers = prompt, black markers = emission, solid line = fit = convolution of exponential function and instrument prompt): (a) pH = 6.7, 450-nm (green) signal fit with monoexponential τ = 21.1 ns. (b) pH = 11.0, 425-nm (magenta) signal fit with monoexponential τ = 9.0 ns.

Kinetic modeling: fitting parameters of 8N2OH

Table SI_3. Lifetime parameters (τ) of sample 8N2OH data set determined at each pH from global fitting of TCSPC data collected at select wavelengths in the 350 nm – 525 nm range. The shaded region of the table was used for the excited cation-zwitterion equilibrium state model.

pH	τ_1 (s)	τ_2 (s)	τ_3 (s)	τ_4 (s)
0.6	2.12e-10	5.04e-9		
1.0	3.42e-10	5.53e-9		
1.7	6.00e-10	6.58e-9		
2.0	7.09e-10	7.19e-9		
4.1	8.78e-10	7.90e-9	1.93e-8	
6.5			2.01e-8	
9.5			1.94e-8	11.7e-9
11.3				11.8e-9

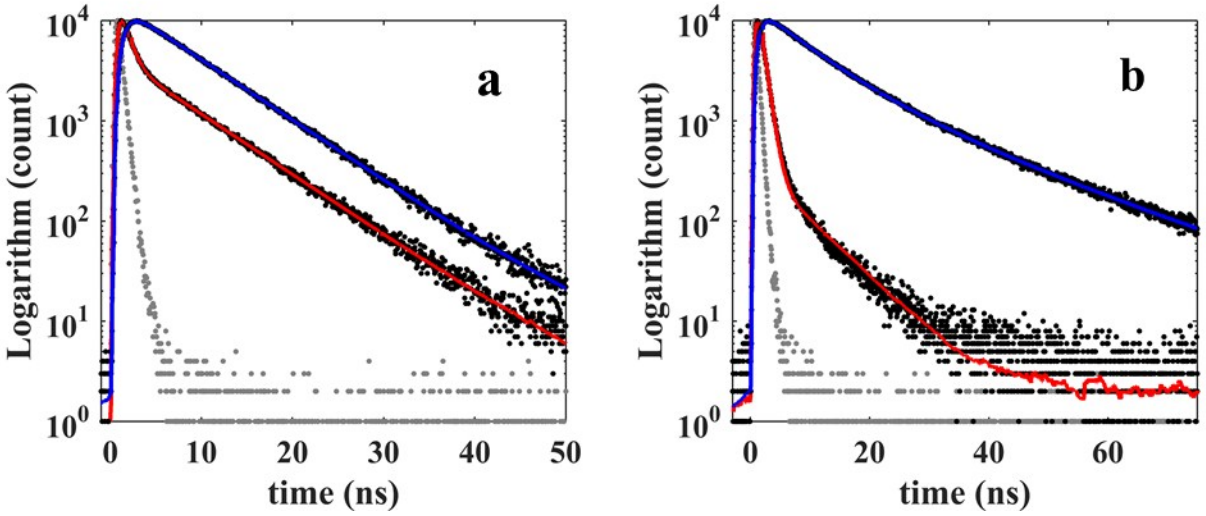


Figure SI_6. Select single wavelength emission decays at 350 nm (cation) and 425 nm (zwitterion) from TRES collected at low pH for 8N2OH (gray markers = prompt, black markers = emission, solid line = fit = convolution of exponential function and instrument prompt): (a) pH = 2.0, 350-nm (red) and 425-nm (blue) signal fits with biexponential function τ_1 = 709 ps and τ_2 = 7.20 ns. (b) pH = 4.1, 350-nm (red) and 425-nm (blue) signal fits with biexponential and triexponential functions τ_1 = 878 ps, τ_2 = 7.9 ns, and τ_3 = 19.3 ns, respectively.

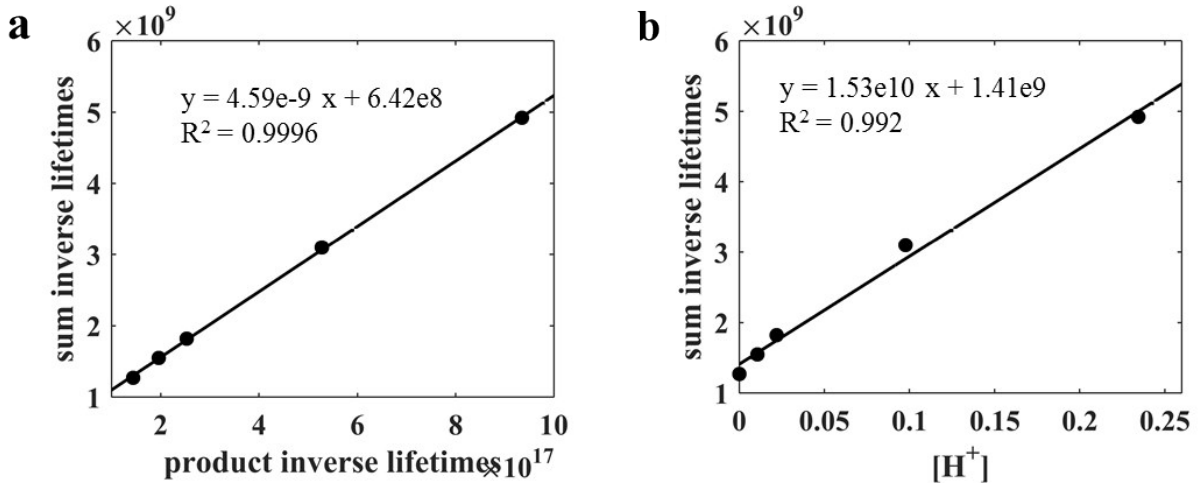


Figure SI_7. Linear plot analysis of the lifetimes from Table SI_3 to provide preliminary estimates of the k_A and k_a parameters of 8N2OH (a) sum of inverse lifetimes ($\tau_1^{-1} + \tau_2^{-1}$) vs. product of inverse lifetimes ($\tau_1^{-1}\,\tau_2^{-1}$) where slope = k_A^{-1}); (b) sum of inverse lifetimes ($\tau_1^{-1} + \tau_2^{-1}$) vs. concentration of H^+ where slope = k_r.

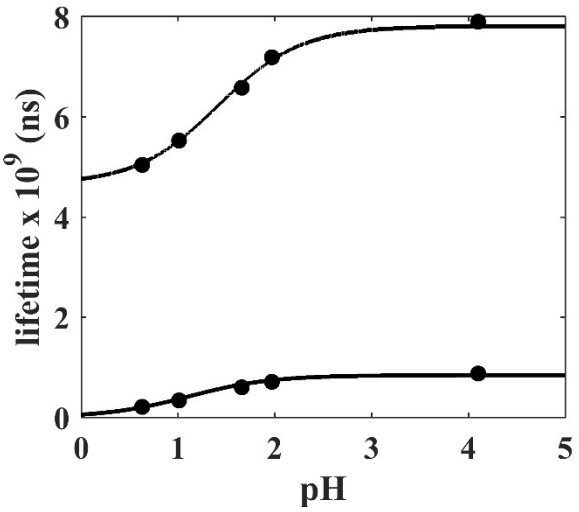


Figure SI_8. Lifetime vs. pH curves generated from fitting lifetime parameters (τ_1, τ_2) of 8N2OH from Table SI 3 to equation 3. The following kinetic parameters were obtained: k_A = 2.15e8, k_B = 1.28e8, k_r = 1.6e10, and k_d = 9.7e8 (pK_a^* = 1.2).

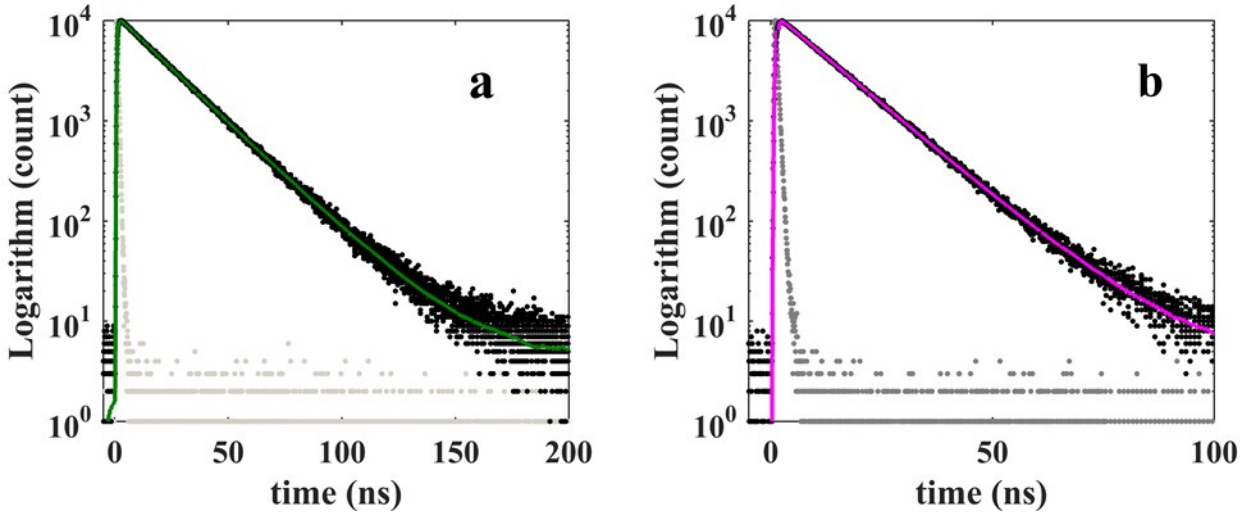


Figure SI_9. Select single wavelength emission decay at 450 nm (neutral) and 425-nm (anion) from TRES collected for 8N2OH (gray markers = prompt, black markers = emission, solid line = fit = convolution of exponential function and instrument prompt): (a) pH = 6.5, 450-nm (green) signal fit with monoexponential τ = 20.1 ns. (b) pH = 11.3, 425-nm (magenta) signal fit with monoexponential τ = 11.8 ns.

Table SI_4. Kinetic parameters obtained from fitting the TCSPC data of 8N2OH to a two-state ESPT model. Kinetic parameters of 2OH and 8CN2OH from literature have also been included for comparison. The relaxation rate constants and estimated pK_a^* of the neutral-anion equilibrium of 8N2OH are included here for completion.

	8N2OH cation-zwitterion	**8N2OH neutral-anion**	**2OH neutral-anion[a,b]**	**8CN2OH neutral-anion[c]**
k_A (s^{-1})	2.15±0.1 × 10^8	5.0 × 10^7	1.38 × 10^8	--
k_B (s^{-1})	1.3±0.1 × 10^8	8.5 × 10^7	1.06 × 10^8	--
k_r ($M^{-1}s^{-1}$)	1.6±0.5 × 10^{10}	--	4.70 × 10^{10} 4.6±0.4 × 10^{10}	--
k_d (s^{-1})	0.97±0.1 × 10^9	--	7.00 × 10^7 7.5±0.6 × 10^7	2.7 × 10^{10}
pK_a^*	1.2±0.2	9.5±0.2	2.8 2.78±0.04	-0.76

[a]Ref 19; [b]Ref 20; proton quenching pathways were explicitly included in the photochemical scheme; [c]Ref 24; in the geminate recombination model, k_r is reported for 8CN2OH as 4 × 10^{10} Å s^{-1}.

Kinetic modeling: fitting parameters of 5N2OMe

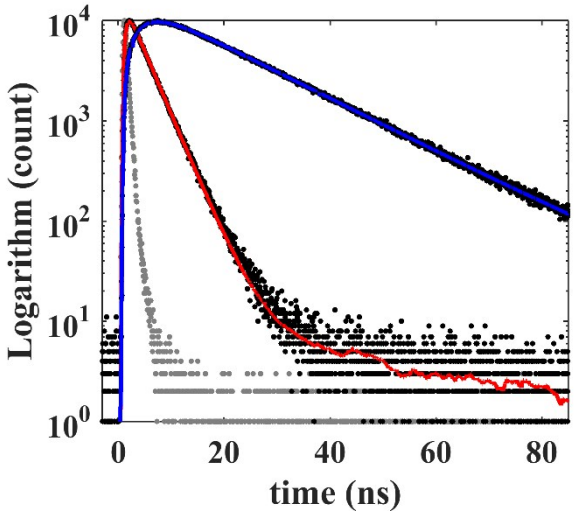


Figure SI_10. Select single wavelength emission decays at 350 nm (cation, blue) and 450 nm (neutral, red) from TRES collected at pH = 2.85 for 5N2OMe (gray markers = prompt, black markers = emission, solid line = fit = convolution of exponential function and instrument prompt). The signals corresponded to biexponential functions τ_1 = 3.42 ns and τ_2 = 16.3 ns.

Table SI_5. Lifetime parameters (τ) of sample 5N2OMe data set determined at each pH from global fitting of TCSPC data collected at select wavelengths in the 350 nm – 525 nm range. The samples were not degassed for these measurements.

pH	τ_1 (s)	τ_2 (s)
1.7	3.03e-9	5.03e-9
2.0	3.26e-9	8.61e-9
2.35	3.36e-9	1.23e-8
2.85	3.42e-9	1.63e-8
3.4	3.52e-9	1.82e-8
3.8	3.59e-9	1.88e-8
4.0	3.57e-9	1.90e-8
4.4	3.57e-9	1.91e-8

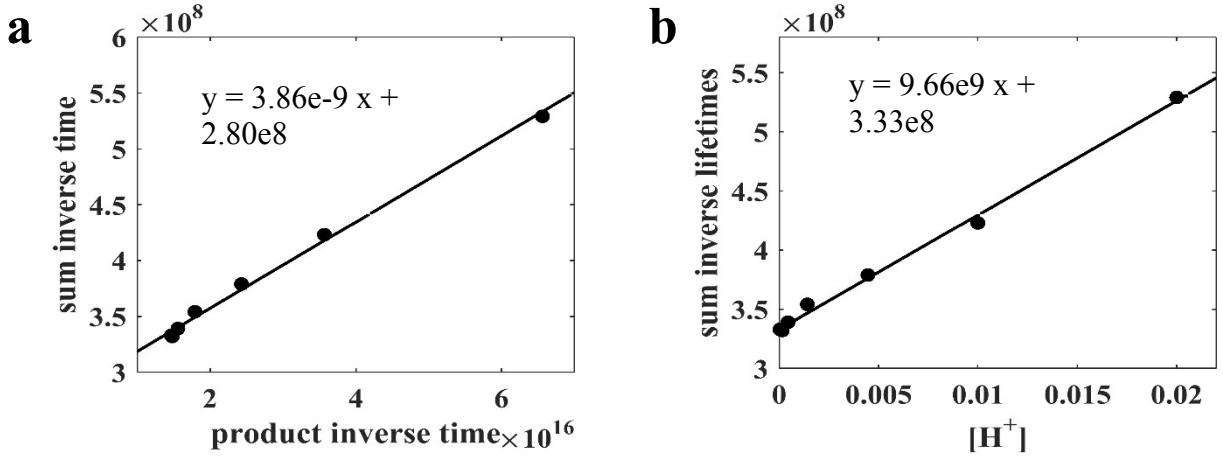
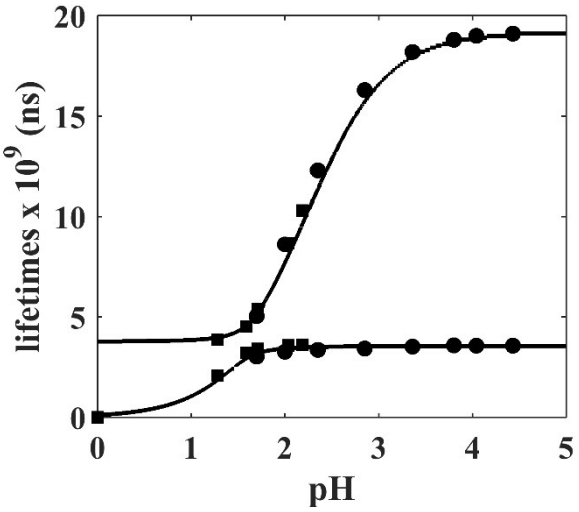


Figure SI_11. Linear plot analysis of the lifetimes from Table SI_6 to provide preliminary estimates of the k_A and k_r parameters of 5N2OMe (a) sum of inverse lifetimes ($\tau_1^{-1} + \tau_2^{-1}$) vs. product of inverse lifetimes ($\tau_1^{-1}\ \tau_2^{-1}$) where slope = k_A^{-1}); (b) sum of inverse lifetimes ($\tau_1^{-1} + \tau_2^{-1}$) vs. concentration of H^+ where slope = k_r.



	5N2OMe cation-neutral
k_A (s^{-1})	$2.65\pm0.1 \times 10^8$
k_B (s^{-1})	$5.2\pm0.1 \times 10^7$
k_a (M^{-1} s^{-1})	$8.8\pm1.0 \times 10^9$
k_d (s^{-1})	$1.7\pm1.0 \times 10^7$
pK_a^*	2.7±0.2

Figure SI_12. Lifetime vs. pH curves generated from fitting lifetime parameters (τ_1, τ_2) of 5N2OMe from Table SI 5 to equation 3. Additional data were collected in a separate experiment and marked as squares in the figure. The following kinetic parameters were obtained: k_A = 2.65e8, k_B = 5.22e7, k_r = 8.80e9, and k_d = 1.70e7 (pK_a^* = 2.70). The range of kinetic parameters that fit the ESPT model of 5N2OMe have been summarized.

Computational results

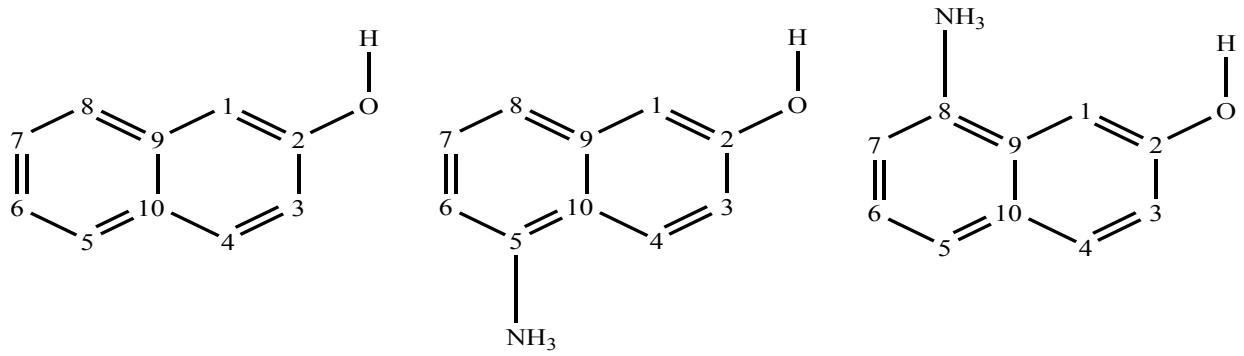


Figure SI_13. Numbering scheme of 2OH, 5N2OH, and 8N2OH as used in tables of computational results.

Table SI_6. Calculated bond lengths (Å) of C-OH, C-O, C-NH_3, and C-NH_2 of the ground (S_0) and excited (S_1, *) protonation states of 2OH and 8N2OH.

Bond S_0, S_1	**2OH neutral**	**2OH anion**	**8N2OH cation**	**8N2OH zwitterion**	**8N2OH neutral**	**8N2OH anion**
C-OH C-OH*	1.372 1.351	--	1.363 1.341	--	1.373 1.374	--
C-O C-O*	--	1.294 1.282	--	1.283 1.277	--	1.294 1.285
C-NH_3 C-NH_3^*	--	--	1.481 1.473	1.481 1.476	--	--
C-NH_2 C-NH_2^*	--	--	--	--	1.402 1.354	1.410 1.398

Table SI_7. Bond lengths (Å) of the ground (S_0) and excited (S_1) protonation states of 2OH determined from the TD-DFT and DFT B3LYP/6-31++G(d,p) calculations respectively.

	2OH neutral (S_0)	**2OH neutral (S_1)**	**2OH anion (S_0)**	**2OH anion (S_1)**
O-C2	1.3717	1.3510	1.2936	1.2819
C1-C2	1.3801	1.4362	1.4183	1.4469
C2-C3	1.4202	1.3918	1.4564	1.4402
C3-C4	1.3758	1.4170	1.3738	1.3976
C4-C10	1.4241	1.4232	1.4272	1.4268
C10-C5	1.4220	1.4127	1.4184	1.4308
C5-C6	1.3800	1.4296	1.3841	1.4133
C6-C7	1.4188	1.3851	1.4198	1.3954
C7-C8	1.3800	1.4257	1.3811	1.4253
C8-C9	1.4239	1.4176	1.4308	1.4164
C9-C1	1.4226	1.4129	1.4148	1.4202
C9-C10	1.4349	1.4499	1.4414	1.4484

Table SI_8. Bond lengths (Å) of the ground (S_0) and excited (S_1) protonation states of 5N2OH determined from the TD-DFT and DFT B3LYP/6-31++G(d,p) calculations respectively.

	5N2OH cation (S_0)	**5N2OH cation (S_1)**	**5N2OH zwitter. (S_0)**	**5N2OH zwitter. (S_1)**	**5N2OH neutral (S_0)**	**5N2OH neutral (S_1)**	**5N2OH anion (S_0)**	**5N2OH anion (S_1)**
O-C2	1.365	1.3399	1.2862	1.2785	1.3720	1.3778	1.2947	1.2841
N-C5	1.4814	1.4723	1.4852	1.4714	1.3984	1.3538	1.4068	1.4136
C1-C2	1.3807	1.4356	1.4207	1.4429	1.3796	1.4193	1.4174	1.4483
C2-C3	1.4182	1.3972	1.4557	1.4417	1.4170	1.3820	1.4525	1.4357
C3-C4	1.3757	1.4049	1.3731	1.3907	1.3776	1.4373	1.3757	1.4078
C4-C10	1.4225	1.4279	1.4261	1.429	1.4230	1.4183	1.4265	1.4291
C10-C5	1.4204	1.4119	1.4143	1.4289	1.4381	1.4393	1.4329	1.4271
C5-C6	1.3728	1.4251	1.3761	1.4113	1.3906	1.4359	1.3920	1.4204
C6-C7	1.4161	1.3803	1.4183	1.388	1.4119	1.3813	1.4149	1.3932
C7-C8	1.3765	1.4222	1.3769	1.4206	1.3799	1.4121	1.3795	1.4176
C8-C9	1.4239	1.4168	1.4314	1.4173	1.4228	1.4241	1.4310	1.4162
C9-C1	1.4188	1.4109	1.409	1.42	1.4230	1.4273	1.4154	1.4202
C9-C10	1.4367	1.4468	1.4444	1.4418	1.4364	1.4310	1.4417	1.4499

Table SI_9. Bond lengths (Å) of the ground (S_0) and excited (S_1) protonation states of 8N2OH determined from the TD-DFT and DFT B3LYP/6-31++G(d,p) calculations respectively.

	8N2OH cation (S_0)	**8N2OH cation (S_1)**	**8N2OH zwitter. (S_0)**	**8N2OH zwitter. (S_1)**	**8N2OH neutral (S_0)**	**8N2OH neutral (S_1)**	**8N2OH anion (S_0)**	**8N2OH anion (S_1)**
O-C2	1.3627	1.3413	1.2825	1.2766	1.3726	1.3736	1.2941	1.2845
N-C5	1.4810	1.4734	1.4807	1.4763	1.4021	1.3544	1.4099	1.3977
C1-C2	1.3831	1.4433	1.4242	1.4522	1.3812	1.4242	1.4195	1.4503
C2-C3	1.4193	1.3901	1.4583	1.4362	1.4172	1.3844	1.4527	1.4359
C3-C4	1.3730	1.4065	1.3691	1.3929	1.3758	1.4290	1.3739	1.4067
C4-C10	1.4236	1.4244	1.4293	1.4236	1.4242	1.4204	1.4270	1.4254
C10-C5	1.4192	1.4161	1.4122	1.4371	1.4223	1.4193	1.4215	1.4149
C5-C6	1.3787	1.4189	1.3864	1.4009	1.3789	1.4149	1.3808	1.4146
C6-C7	1.4132	1.3904	1.4111	1.4003	1.4134	1.3767	1.4171	1.3874
C7-C8	1.3747	1.4175	1.3773	1.4182	1.3891	1.4391	1.3874	1.4312
C8-C9	1.4218	1.4173	1.4255	1.4114	1.4383	1.4366	1.4430	1.4230
C9-C1	1.4208	1.4093	1.4104	1.4192	1.4235	1.4243	1.4175	1.4189
C9-C10	1.4363	1.4485	1.4437	1.4443	1.4345	1.4385	1.4382	1.4584

Table SI_10. Difference between the calculated Mulliken charges (q_{S1}-q_{S0}) of the OH, O, NH_3, and NH_2 moieties of the excited (S_1) and ground (S_0) protonation states of 2OH and 8N2OH.

	2OH neutral	**2OH anion**	**8N2OH cation**	**8N2OH zwitterion**	**8N2OH neutral**	**8N2OH anion**
OH	0.083	--	0.110	--	-0.004	--
O	--	0.207	--	0.186	--	0.177
NH_3	--	--	-0.026	-0.031	**--**	--
NH_2	--	--	--	--	0.169	-0.006

Table SI_11. Mulliken charge (q) of ground (S_0) and excited (S_1) state naphthol and naphtholate C ring atoms and OH/O moieties determined from the TD-DFT and DFT B3LYP/6-31++G(d,p) calculations, respectively.

	2OH neutral (S_0)	**2OH neutral (S_1)**	**2OH anion (S_0)**	**2OH anion (S_1)**
OH/O	-0.3875	-0.3044	-0.8345	-0.6278
C1	0.075	0.166	0.3173	0.3450
C2	0.138	0.110	-0.2267	-0.1602
C3	0.019	-0.024	0.4232	0.3257
C4	0.014	0.080	-0.1449	-0.0653
C10	-0.307	-0.491	-0.5905	-0.6642
C5	-0.046	-0.037	0.0376	-0.1258
C6	-0.016	0.031	-0.1240	0.0141
C7	-0.103	-0.163	-0.0503	-0.2146
C8	-0.147	-0.067	0.0812	0.0798
C9	-0.327	-0.403	-0.6288	-0.6339

Table SI_12. Mulliken charge (*q*) of ground (S_0) and excited (S_1) protonation states of 5N2OH C ring atoms and OH/O and NH_3/NH_2 moieties determined from the TD-DFT and DFT B3LYP/6-31++G(d,p) calculations, respectively.

	5N2OH cation (S_0)	**5N2OH cation (S_1)**	**5N2OH zwitter. (S_0)**	**5N2OH zwitter. (S_1)**	**5N2OH neutral (S_0)**	**5N2OH neutral (S_1)**	**5N2OH anion (S_0)**	**5N2OH anion (S_1)**
OH/O	-0.1314	-0.0036	-0.8061	-0.6003	-0.1521	-0.1666	-0.8418	-0.6397
NH_3/NH_2	0.8910	0.8425	0.8575	0.7808	0.1283	0.2913	0.0971	0.0259
C1	0.2074	0.3023	0.2193	0.2099	0.1206	-0.1028	0.1417	0.1188
C2	0.2993	0.2673	0.0990	0.1358	0.2660	0.0595	0.0530	0.0880
C3	-0.0223	-0.0424	0.1880	0.1348	-0.1735	-0.1317	0.0297	-0.0443
C4	-0.1426	0.0004	-0.0833	-0.0047	-0.0845	-0.5823	-0.0263	0.0371
C10	-0.4604	-0.7104	-0.9146	-1.0386	-0.4496	0.3516	-0.9109	-1.0222
C5	-0.1839	-0.1097	0.0267	0.0466	0.0118	-0.3774	0.1721	0.2987
C6	0.5583	0.4888	0.5021	0.3885	0.5487	0.1921	0.4537	0.4732
C7	-0.2748	-0.3070	-0.2812	-0.3340	-0.2025	-0.3106	-0.1641	-0.3037
C8	-0.0730	0.0069	0.0714	0.0864	-0.1130	-0.2766	0.0119	0.0700
C9	-0.4327	-0.4942	-0.5440	-0.4648	-0.6083	0.3430	-0.6328	-0.7462

Table SI_13. Mulliken charge (*q*) of ground (S_0) and excited (S_1) protonation states of 8N2OH C-ring atoms and OH/O and NH_3/NH_2 moieties determined from the TD-DFT and DFT B3LYP/6-31++G(d,p) calculations, respectively.

	8N2OH cation (S_0)	**8N2OH cation (S_1)**	**8N2OH zwitter. (S_0)**	**8N2OH zwitter. (S_1)**	**8N2OH neutral (S_0)**	**8N2OH neutral (S_1)**	**8N2OH anion (S_0)**	**8N2OH anion (S_1)**
OH/O	-0.1234	-0.0132	-0.7878	-0.6021	-0.1517	-0.1555	-0.8380	-0.6611
NH_3/NH_2	0.8923	0.8668	0.8366	0.8053	0.1303	0.2996	0.0869	0.0805
C1	-0.2331	-0.0156	0.1042	0.0973	-0.0919	-0.5158	-0.0126	-0.0578
C2	0.0684	0.1427	-0.0956	-0.1108	0.0029	-0.0317	-0.1883	-0.1289
C3	0.0911	0.0827	0.4193	0.3761	0.1012	0.0350	0.3214	0.2009
C4	0.1793	0.0801	0.1164	0.1798	0.0947	-0.1104	0.1072	0.0851
C10	-0.0189	-0.4078	-0.8084	-0.9214	-0.6898	-0.0338	-0.9676	-0.9695
C5	-0.1197	0.0821	0.1300	0.0182	0.0742	-0.1339	0.0468	0.0210
C6	-0.3813	-0.2513	-0.2906	-0.1958	-0.2033	-0.3262	-0.2117	-0.1468
C7	0.0952	0.4419	0.3654	0.2118	0.5343	0.0781	0.3509	0.3216
C8	-0.4621	-0.3026	0.1169	0.0900	-0.0421	-0.3086	0.1253	0.1465
C9	0.2362	-0.4671	-0.7736	-0.6251	-0.4810	0.4899	-0.4440	-0.5308

Hammett equation: fitting 5-x-2OH

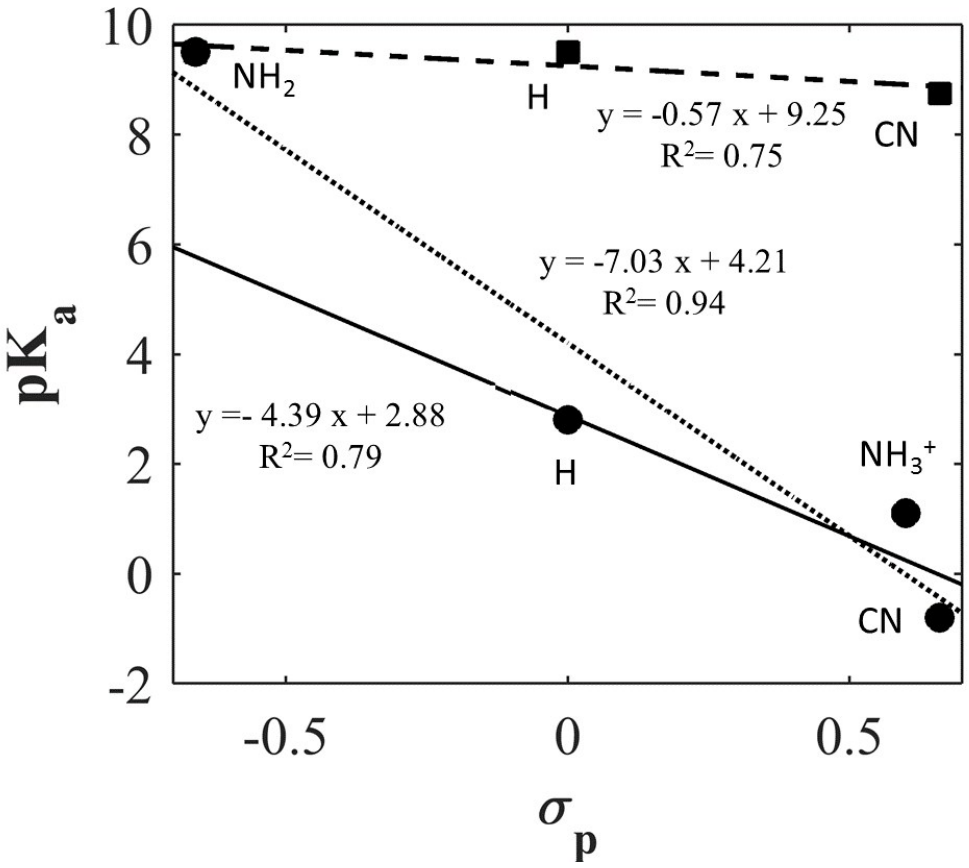


Figure SI_14. Hammett equation fits to 5-*x*-2OH acidity, where *x* = CN, H, NH_2, and NH_3^+. Ground and excited state pK_a values are represented by square and circular markers. The solid and dotted lines represent the Hammett equation fits to the excited state pKa^*: x = H, CN, and NH_3^+ and x = H, CN, NH_3^+, and NH_2, respectively. The dashed line is the Hammett equation fit to the ground state pK_a: x = H, CN, and NH_2.