Hydroxybenzo[*b*]quinolizinium Ions: Water-Soluble and Solvatochromic Photoacids

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Supporting Information

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1. NMR spectra of compounds 4a-BF_4, 2a, 1a and 1d.

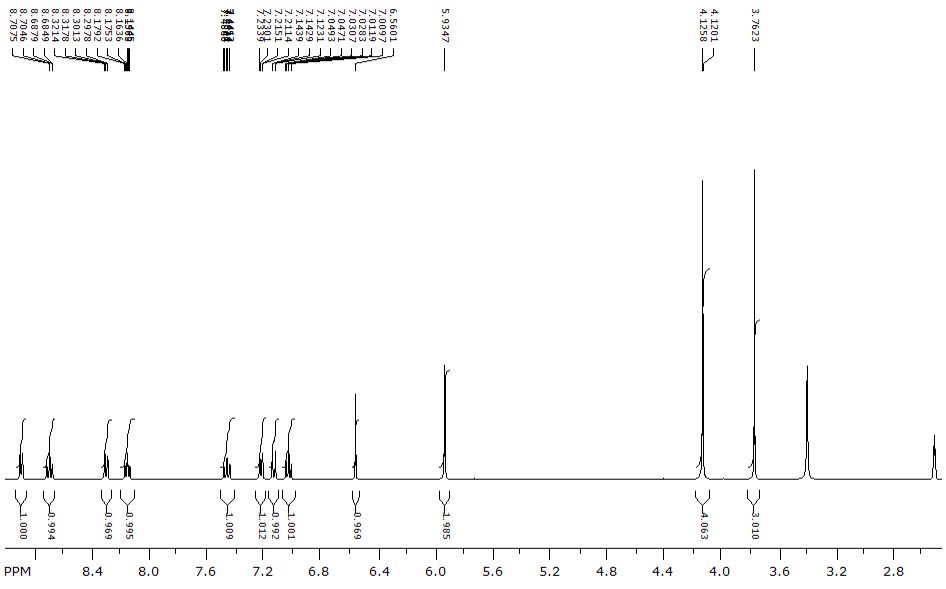

Figure S1. [1]H-NMR spectrum (400 MHz) of **4a-BF_4** in d_6-DMSO.

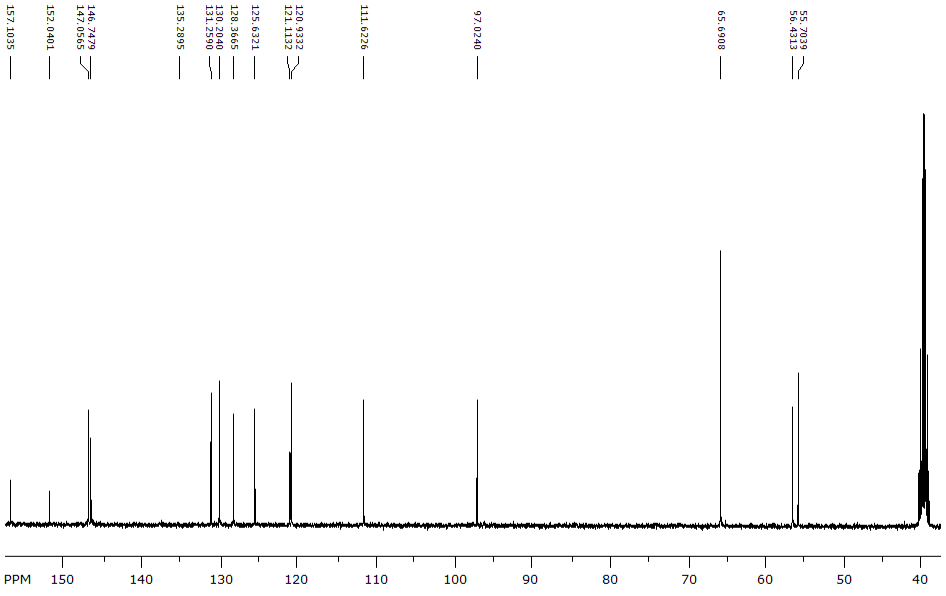

Figure S2. [13]C-NMR spectrum (100 MHz) of **4a-BF_4** in d_6-DMSO.

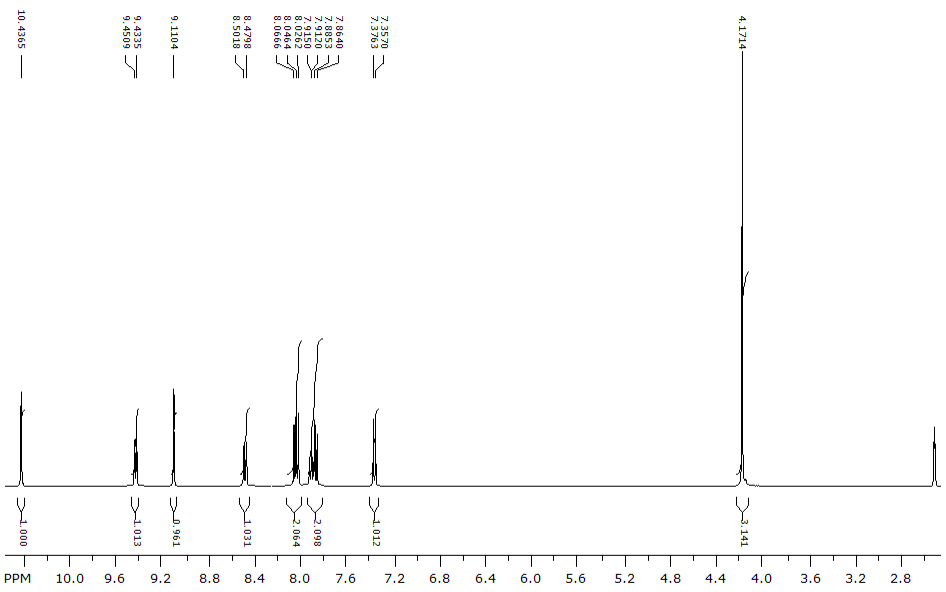

Figure S3. [1]H-NMR spectrum (400 MHz) of **2a** in d_6-DMSO.

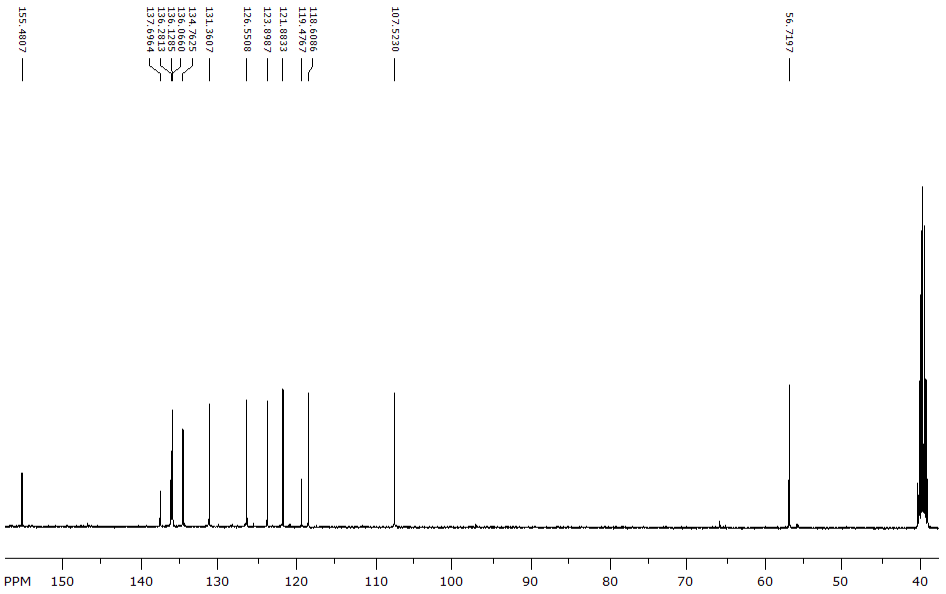

Figure S4. [13]C-NMR spectrum (100 MHz) of **2a** in d_6-DMSO.

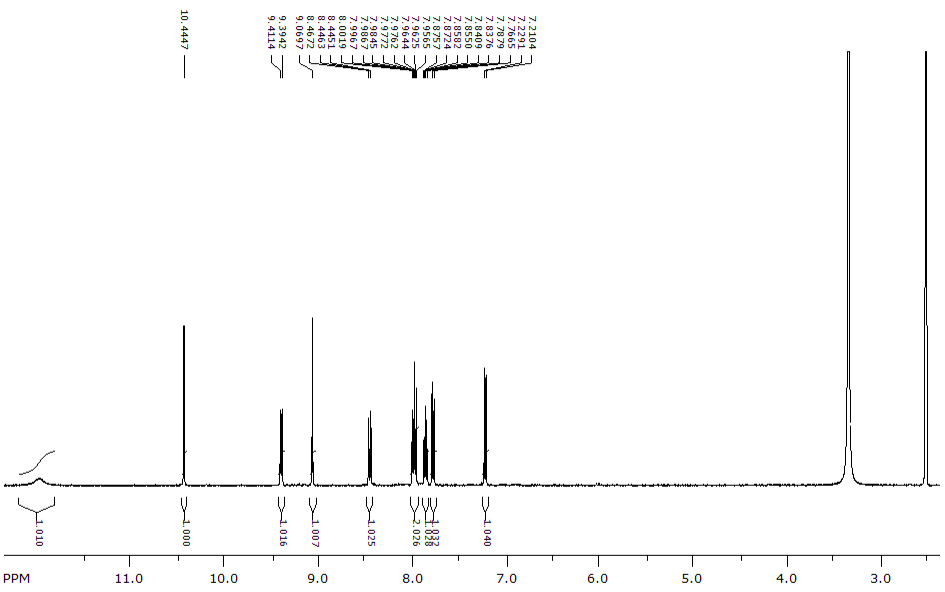

Figure S5. ^{1}H-NMR spectrum (400 MHz) of **1a** in d_6-DMSO.

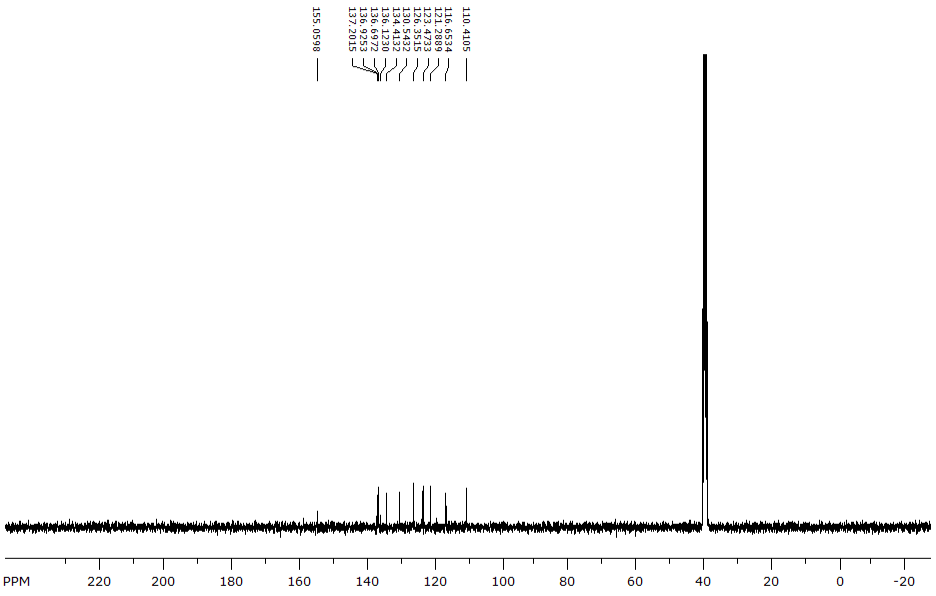

Figure S6. ^{13}C-NMR spectrum (100 MHz) of **1a** in d_6-DMSO.

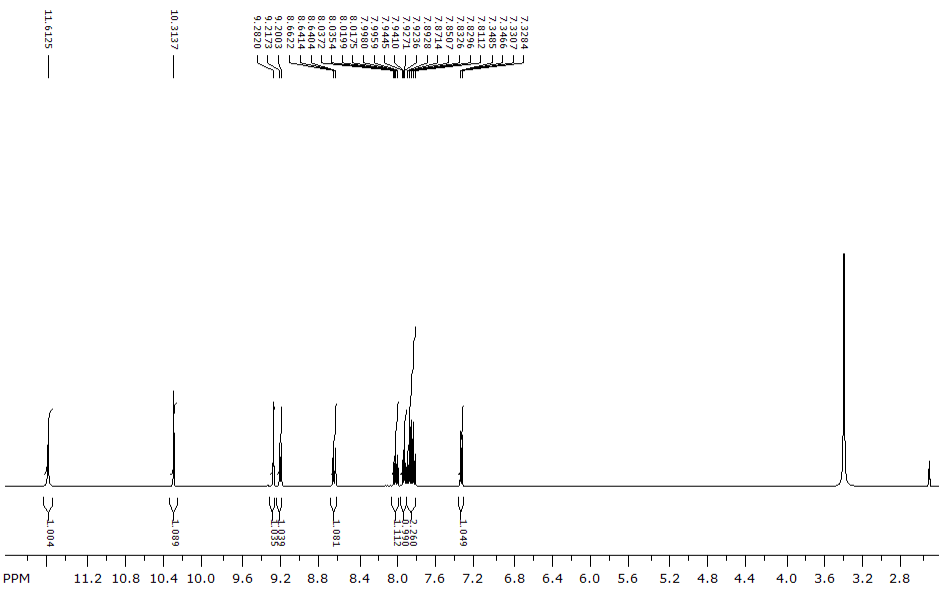

Figure S7. [1]H-NMR spectrum (400 MHz) of **1d** in d_6-DMSO.

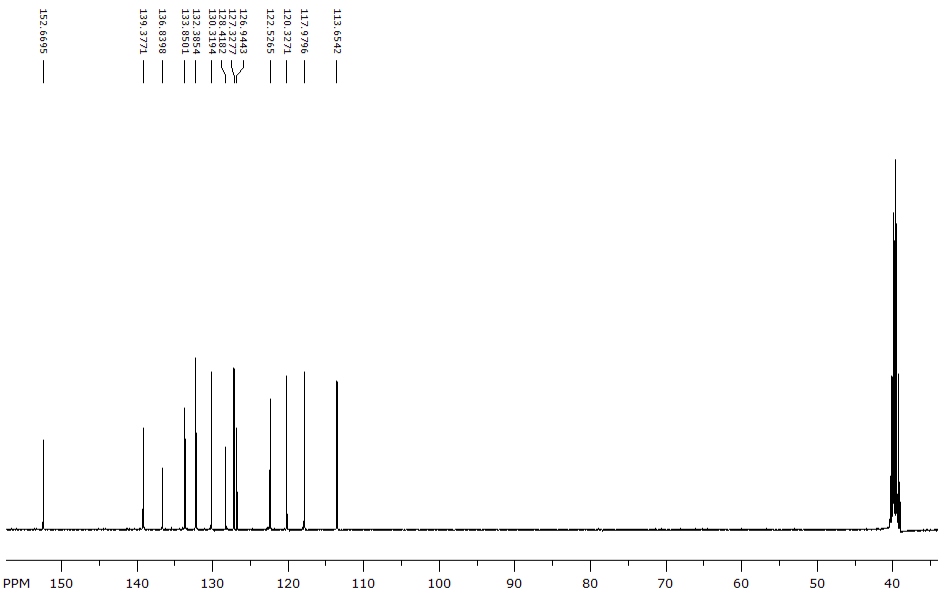

Figure S8. [13]C-NMR spectrum (100 MHz) of **1d** in d_6-DMSO.

2. Absorption and emission spectra in different solvents

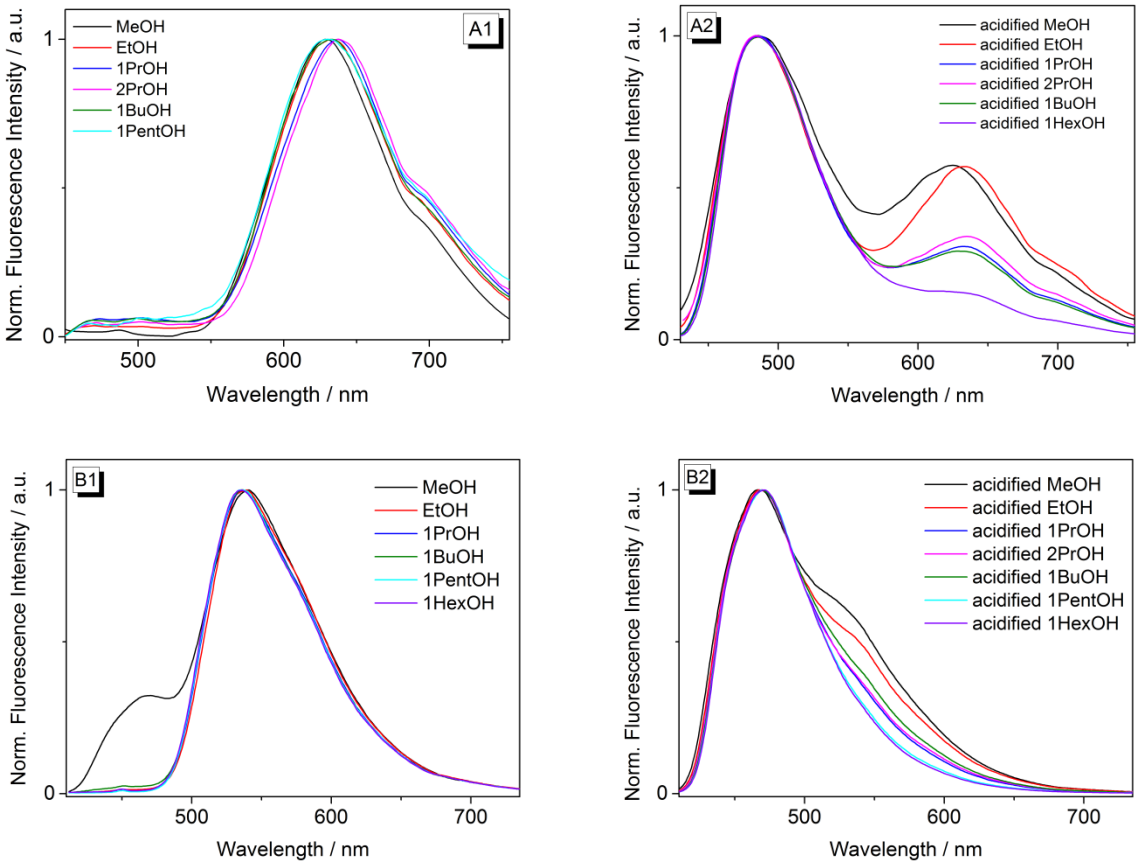

Figure S9. Normalized fluorescence spectra of **1b** (A1) (λ_{ex} = 396 nm) and **1c** (B1) (λ_{ex} = 395 nm) in different alcohols in the absence (1) and in the presence of trifluoroacetic acid (2); (A2: λ_{ex} = 361 nm; B2: λ_{ex} = 376 nm; $c = 10^{-5}$ M).

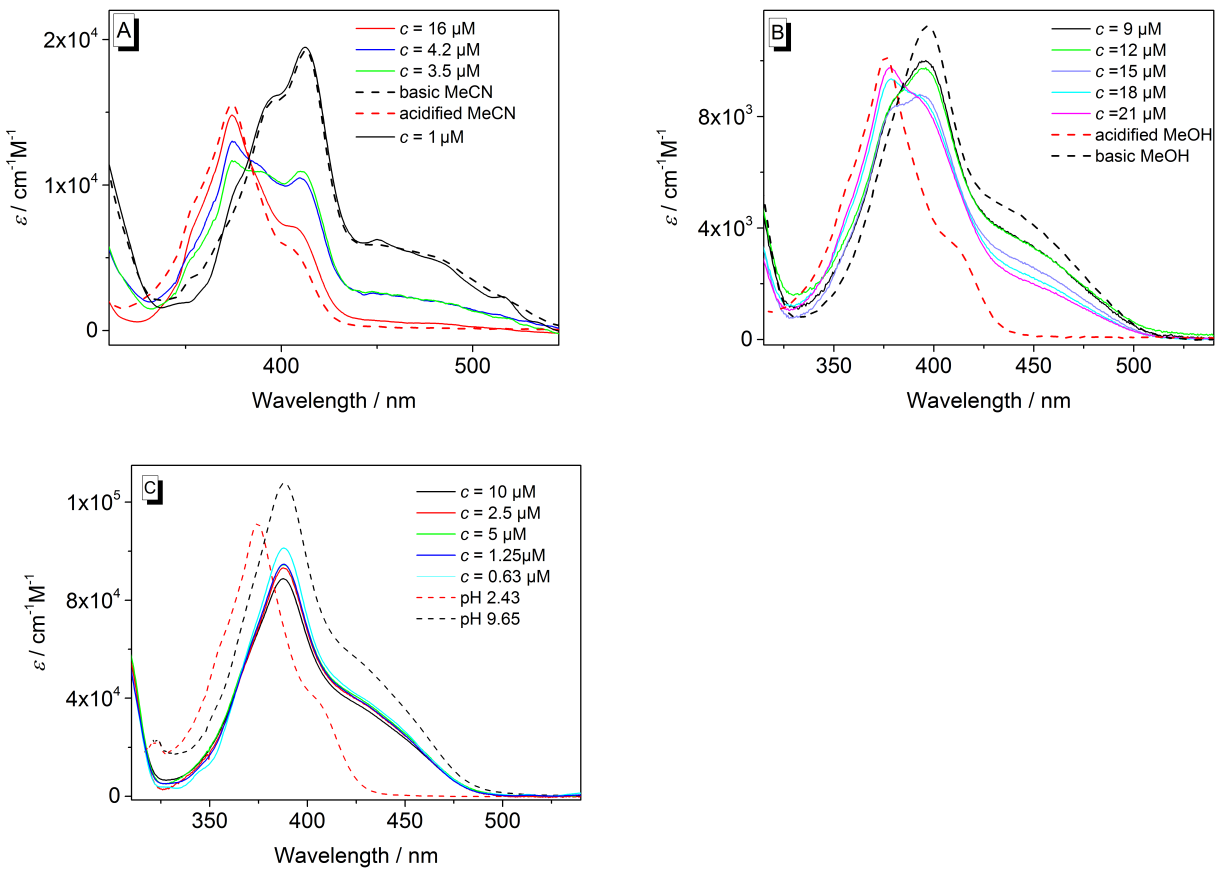

Figure S10. Absorption spectra of the solutions of **1c** at different concentrations in MeCN (A), MeOH (B), and water (C). For comparison absorption spectra under acidic and alkaline conditions are also presented (dashed lines).

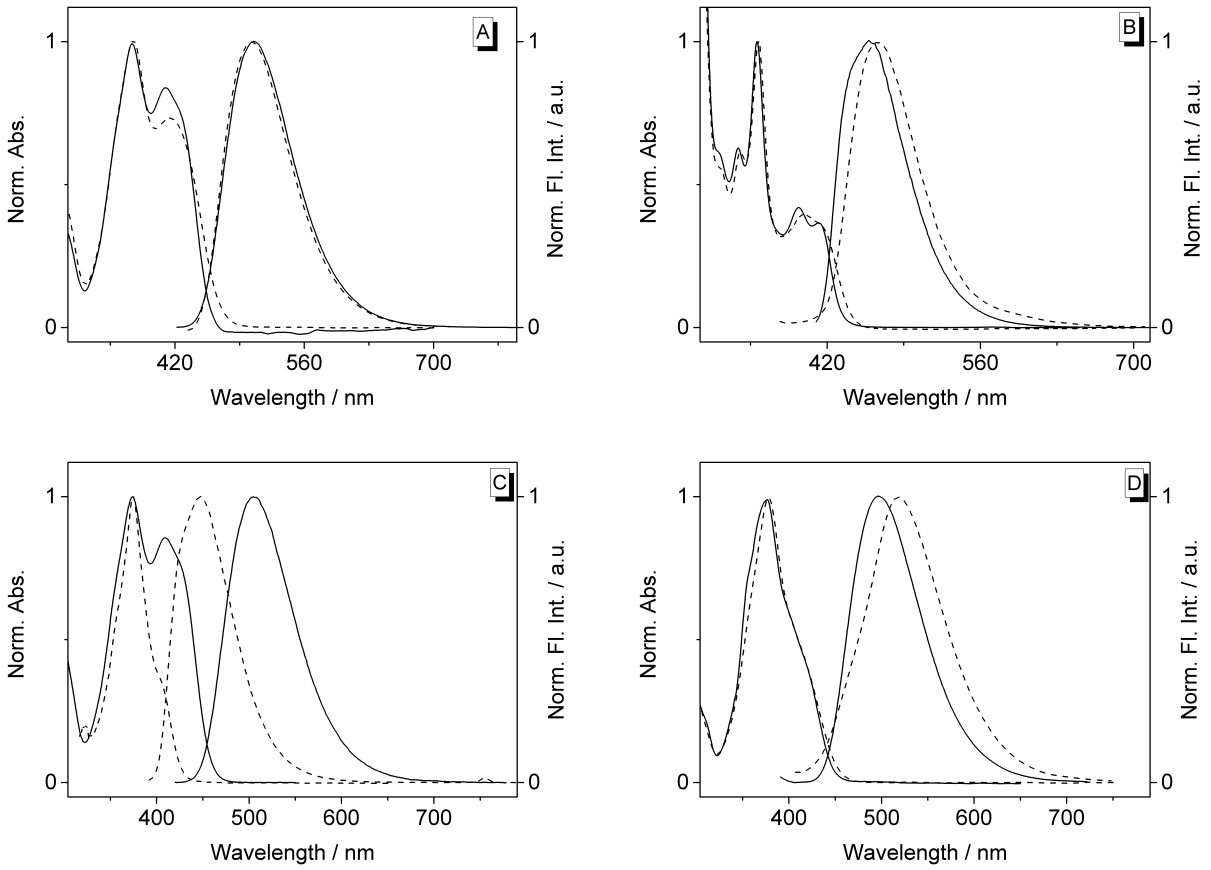

Figure S11. Normalized absorption and fluorescence spectra of **1a** and **2a** (A), **1b** and **2b** (B), **1c** and **2c** (C), and **1d** and **2d** (D) in Britton-Robinson buffer at low pH (**1a–d**; dashed line) or in MeOH (**2a–d**, solid line).

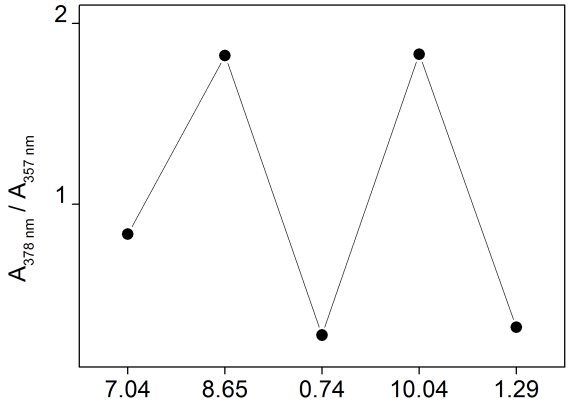

Figure S12. Absorption ratio A_{378} / A_{357} of **1b** (c = 10 μM) in Britton-Robinson buffer as obtained from consecutive addition of acid and base.

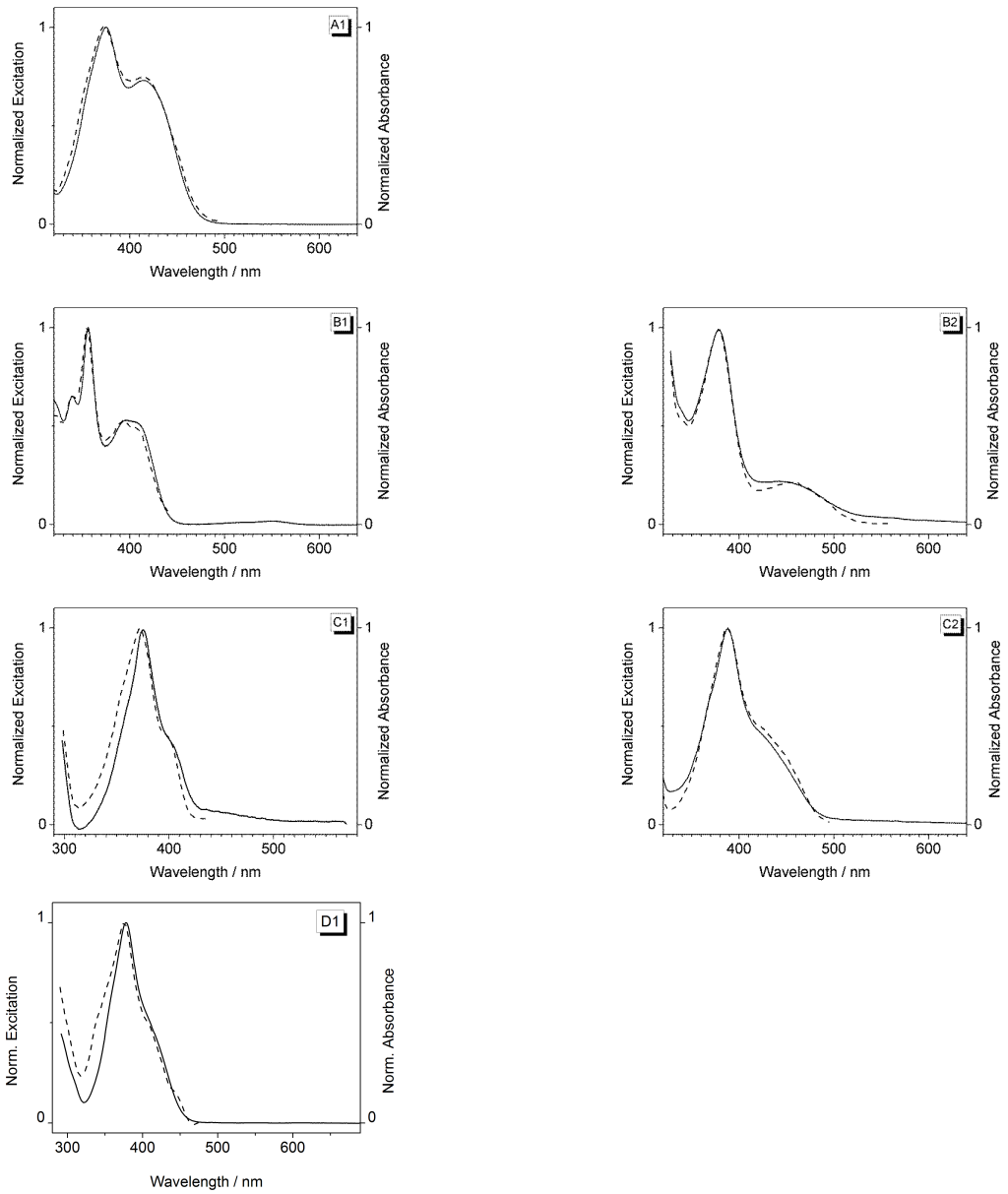

Figure S13. Normalized absorption spectra (solid line) and normalized excitation spectra (dashed line) of **1a** (A), **1b** (B), **1c** (C), and **1d** (D) under acidic (1) and alkaline (2) conditions. Acidic conditions in Britton-Robinson buffer (absorption of **1a**,**d**,) or in aq. 11.8 M $HClO_4$ (absorption and excitation of **1b**,**c**; excitation of **1a**,**d**); alkaline conditions in Britton-Robinson buffer with addition of 20 μL 2 M NaOH. Excitation spectra were recorded from solutions with $c = 10^{-5}$ M and λ_{em} = 508 nm (**1a**, acidic), λ_{em} = 459 nm (**1b**, acidic) λ_{em} = 448 nm (**1c**, acidic). λ_{em} = 528 nm (**1c**, alkaline), and λ_{em} = 507 nm (**1d**, acidic).

3. Determination of pK_a^* values

Emission spectra were recorded in $HClO_4$ solutions and in neutral or aq. NaOH solutions to obtain the spectra of the acids **1a**–**1c** and their conjugate bases **1a**^{cB}–**1c**^{cB}. In the case of **1a**^{cB} the emission maximum could not be determined from the original spectrum (as it partially overlaps with the emission of the acid) and was obtained by deconvolution analysis (Figure S12). The energy of the 0-0 transition was obtained from the intersection of the normalized absorption and emission spectra. The excited-state acidity constant pK_a^* was estimated according to the Förster cycle (Eq. 1).

$$\Delta pK = 0.00209\,[\tilde{\nu}\,(\mathrm{cB}) - \tilde{\nu}\,(\mathrm{ArOH})]\ /\ \mathrm{cm}^{-1} \qquad (\text{Eq. 1})$$

$\tilde{\nu}$ (cB) = Energy of the 0-0 transition of the conjugate base, in wavenumbers

$\tilde{\nu}$ (ArOH) = Energy of the 0-0 transition of the acid (hydroxyarene), in wavenumbers

Table S1. Emission energies of **1a**–**1c** and **1a**^{cB}–**1c**^{cB} used for Förster-cycle calculations

	$\tilde{\nu}$ (ArOH) / cm^{-1}	$\tilde{\nu}$ (cB) / cm^{-1}	pK_a^*
1a	22272	18553	–1
1b	23202	19646	0
1c	24450	21142	–1

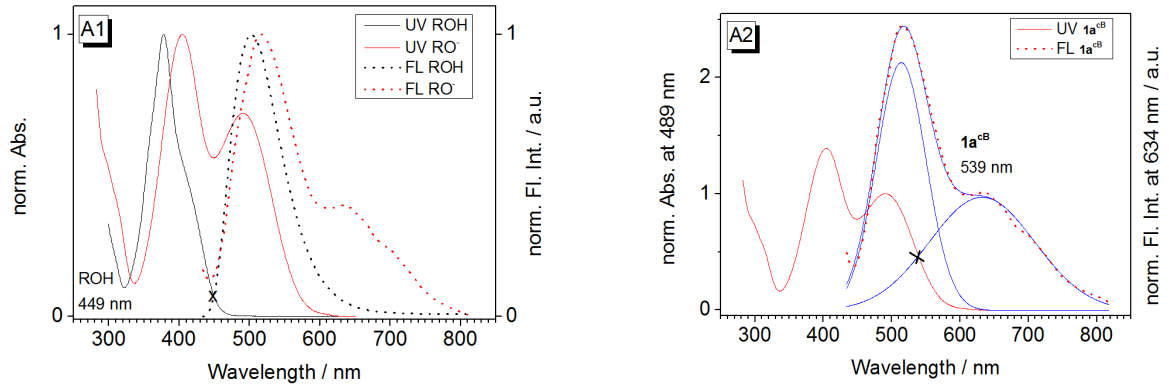

Figure S14. A1: Absorption (solid line) and emission spectra (dotted line) of **1a** (c = 10^{-5} M, λ_{ex} = 373 nm) in $HClO_4$ (11.8 M) (black) and in Britton-Robinson buffer at pH 8.63 (red, λ_{ex} = 402 nm). A2: Normalized absorption (red solid line) and emission spectra (red dotted line) of **1a** used for multiple curve deconvolution of the emission spectra of **1a**^{cB} (blue line).

4. Computational studies

DFT calculations were performed using Gaussian 09 Rev. D.01.[1] For the gas-phase calculations, a hybrid CAM-B3LYP functional with a D95V basis set was used. Excited-state dipole moments were calculated using the CI density in TD-DFT calculations. The charge-transfer indices q_{CT} and D_{CT} were calculated with Multiwfn v. 3.3.8, using the S_0 geometries and wavefunctions generated from DFT (S_0) and TD-DFT (S_1) calculations.[2]

The calculations in aqueous medium were performed using the CAM-B3LYP functional with a 6-31+G(d,p) basis set. The bulk solvent effects were included by the polarizable continuum model in its conductor-like version (CPCM, water). An $(H_2O)_3$ cluster was manually placed in the vicinity of the hydroxyl group, and full geometry optimization was performed in ground state and in the first excited state. The obtained stationary points were checked for the absence of imaginary frequencies.

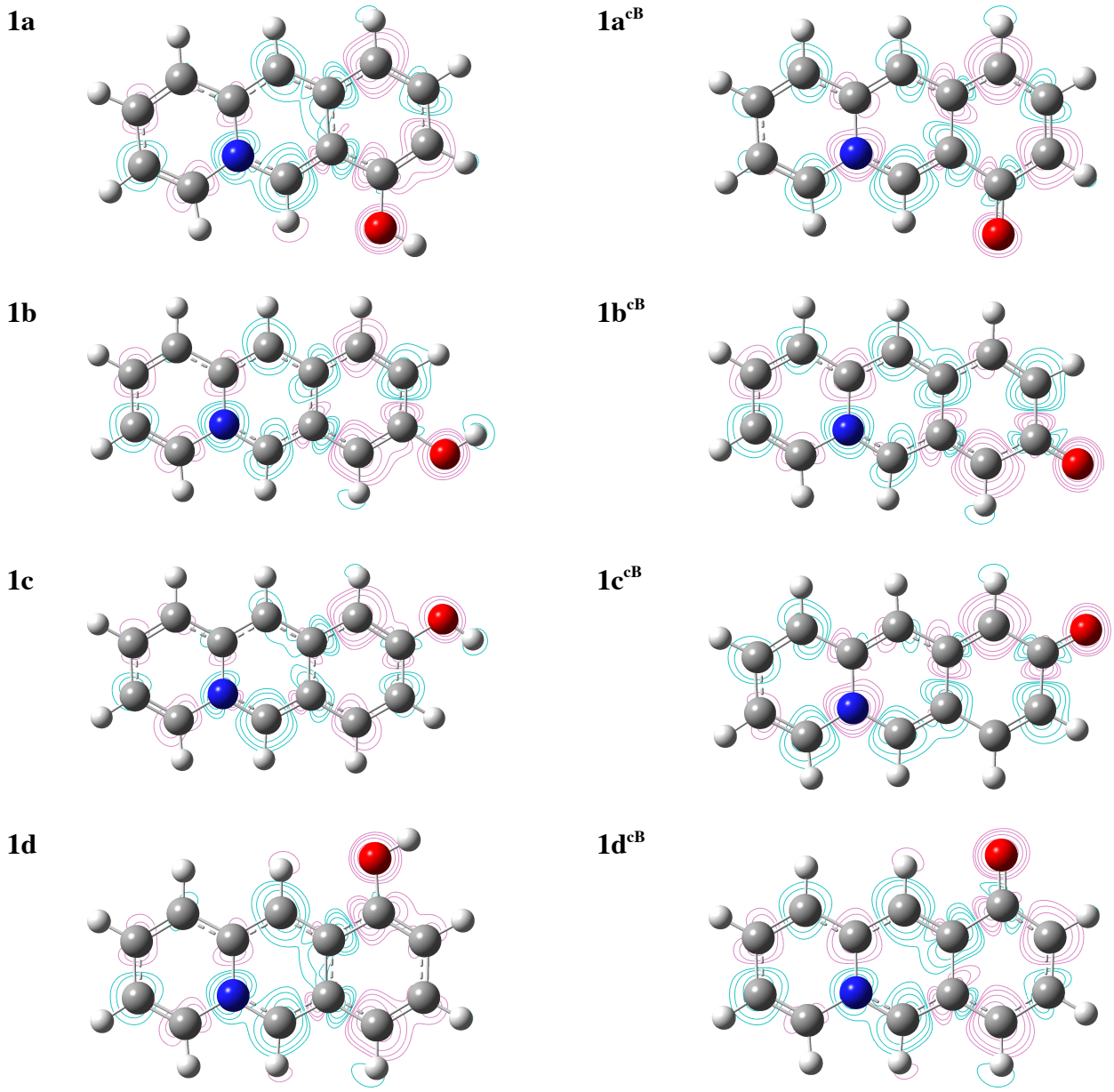

Figure S15. Electron density difference plots [ϱ(S_1) −ϱ(S_0)] corresponding to the $S_0 \rightarrow S_1$ electronic excitation of **1a–d** and **1a^{cB}–1d^{cB}**. Red regions correspond to the *decrease* of (negative) electron density upon excitation; cyan regions correspond to the *increase* of electron density upon excitations.

Table S2. Atom Coordinates of **1a** [a]

Tag	Symbol	X	Y	Z
1	C	-3.9140910	–0.4832330	–0.0000060
2	C	–3.7044360	0.9378570	0.0000020
3	C	–2.4430590	1.4431430	0.0000080
4	N	–1.3198720	0.5938430	0.0000060
5	C	–1.4920950	–0.8027990	–0.0000020
6	C	–2.8308780	–1.3178680	–0.0000080
7	C	–0.0658220	1.1380140	0.0000090
8	C	1.0679900	0.3432190	0.0000080
9	C	0.9393890	–1.0923100	0.0000040
10	C	–0.3620890	–1.6207080	–0.0000020
11	C	2.3804850	0.9342440	0.0000040
12	C	3.4973240	0.1342770	–0.0000090
13	C	3.3530160	–1.2889470	0.0000050
14	C	2.1167870	–1.8968160	0.0000070
15	H	–4.9221060	–0.8805520	–0.0000110
16	H	–4.5450160	1.6208900	0.0000030
17	H	–2.2261520	2.5035940	0.0000120
18	H	–2.9496300	–2.3951790	–0.0000150
19	H	0.0150140	2.2177010	0.0000120
20	H	–0.5120100	–2.6944150	–0.0000070
21	H	2.0285930	–2.9774660	0.0000090
22	H	4.4927480	0.5681240	–0.0000350
23	H	4.2518810	–1.8967040	0.0000020
24	O	2.3848980	2.3109340	–0.0000340
25	H	3.2714880	2.7212070	0.0001420

[a] Absolute energy: E(RCAM-B3LYP) = –630.71968540 a.u.

Table S3. Atom Coordinates of **1a**^{cB} [a]

Tag	Symbol	X	Y	Z
1	C	3.9094660	–0.3486120	0.0000000
2	C	3.6566750	1.0753720	0.0000000
3	C	2.3782690	1.5275140	0.0000000
4	N	1.2870420	0.6458630	0.0000000
5	C	1.4887250	–0.7565050	0.0000000
6	C	2.8602970	–1.2172800	0.0000000
7	C	0.0000000	1.1408490	0.0000000
8	C	–1.1016520	0.3325640	0.0000000
9	C	–0.9489560	–1.1193510	0.0000000
10	C	0.3996860	–1.6004790	0.0000000
11	C	–2.4431170	0.9791170	0.0000000
12	C	–3.5571130	0.0618550	0.0000000
13	C	–3.3644570	–1.3077470	0.0000000
14	C	–2.0801070	–1.9227420	0.0000000
15	H	4.9307840	–0.7127630	0.0000000
16	H	4.4742020	1.7853560	0.0000000
17	H	2.1199990	2.5793720	0.0000000
18	H	3.0165270	–2.2904660	0.0000000
19	H	–0.1316910	2.2180350	0.0000000
20	H	0.5840040	–2.6694520	0.0000000
21	H	–1.9895660	–3.0038770	0.0000000
22	H	–4.5535550	0.4909820	0.0000000
23	H	–4.2408220	–1.9524550	0.0000000
24	O	–2.5506820	2.2458630	0.0000000

[a] Absolute energy: E(RCAM–B3LYP) = –630.30962161 a.u.

Table S4. Atom Coordinates of **1b** [a]

Tag	Symbol	X	Y	Z
1	C	1.6527230	–3.7693970	0.0000000
2	C	2.7976990	–2.9061790	0.0000000
3	C	2.6400030	–1.5550200	0.0000000
4	N	1.3594150	–0.9713070	0.0000000
5	C	0.2192260	–1.7924340	0.0000000
6	C	0.4023420	–3.2125820	0.0000000
7	C	1.2401790	0.3912250	0.0000000
8	C	0.0000000	1.0255960	0.0000000
9	C	–1.1894780	0.2057280	0.0000000
10	C	–1.0406100	–1.1842970	0.0000000
11	C	–0.1094740	2.4470210	0.0000000
12	C	–1.3564620	3.0288190	0.0000000
13	C	–2.5489110	2.2214570	0.0000000
14	C	–2.4668640	0.8535570	0.0000000
15	O	–1.4176130	4.3978240	0.0000000
16	H	1.7841850	–4.8447220	0.0000000
17	H	3.8002010	–3.3165350	0.0000000
18	H	3.4703900	–0.8607560	0.0000000
19	H	–0.4889070	–3.8295290	0.0000000
20	H	2.1649740	0.9552670	0.0000000
21	H	–1.9132860	–1.8280450	0.0000000
22	H	0.7703440	3.0804010	0.0000000
23	H	–3.5203670	2.7094780	0.0000000
24	H	–3.3684470	0.2499160	0.0000000
25	H	–2.3163230	4.7801250	0.0000000

[a] Absolute energy: E(RCAM–B3LYP) = –630.71522580 a.u.

Table S5. Atom Coordinates of **1b**^{cB} [a]

Tag	Symbol	X	Y	Z
1	C	1.6117650	–3.7511250	0.0000000
2	C	2.7588720	–2.8978620	0.0000000
3	C	2.6155080	–1.5421010	0.0000000
4	N	1.3459040	–0.9332840	0.0000000
5	C	0.2008760	–1.7522160	0.0000000
6	C	0.3682940	–3.1642360	0.0000000
7	C	1.2419840	0.4238450	0.0000000
8	C	0.0000000	1.1034550	0.0000000
9	C	–1.1981180	0.2604520	0.0000000
10	C	–1.0580970	–1.1155360	0.0000000
11	C	–0.0976080	2.4910000	0.0000000
12	C	–1.3722500	3.1612390	0.0000000
13	C	–2.5625380	2.2774100	0.0000000
14	C	–2.4804010	0.9182220	0.0000000
15	O	–1.5155790	4.4240570	0.0000000
16	H	1.7268960	–4.8280490	0.0000000
17	H	3.7597360	–3.3137450	0.0000000
18	H	3.4543820	–0.8582270	0.0000000
19	H	–0.5346740	–3.7655430	0.0000000
20	H	2.1741350	0.9753290	0.0000000
21	H	–1.9383140	–1.7506430	0.0000000
22	H	0.7924330	3.1129240	0.0000000
23	H	–3.5223880	2.7876500	0.0000000
24	H	–3.3786160	0.3055550	0.0000000

[a] Absolute energy: E(RCAM–B3LYP) = –630.29473651 a.u.

Table S6. Atom Coordinates of **1c** [a]

Tag	Symbol	X	Y	Z
1	C	–3.9785880	–0.8977670	0.0000140
2	C	–4.0415320	0.5382010	0.0000780
3	C	–2.8984310	1.2718200	0.0000720
4	N	–1.6344050	0.6502530	0.0000130
5	C	–1.5387110	–0.7538020	–0.0000410
6	C	–2.7579170	–1.5122980	–0.0000420
7	C	–0.5021260	1.4192430	0.0000250
8	C	0.7654690	0.8605270	–0.0000440
9	C	0.9041380	–0.5787890	–0.0000570
10	C	–0.2772380	–1.3438710	–0.0000580
11	C	1.9472040	1.6788040	–0.0001270
12	C	3.1846470	1.0966950	–0.0000470
13	C	3.3113560	–0.3386530	0.0000120
14	C	2.1985910	–1.1557790	–0.0000520
15	H	–4.8934550	–1.4782750	0.0000210
16	H	–4.9961650	1.0497870	0.0001410
17	H	–2.8874290	2.3543040	0.0001260
18	H	–2.6704900	–2.5925940	–0.0000790
19	H	–0.6504150	2.4927500	0.0000420
20	H	–0.2228890	–2.4264730	–0.0000960
21	H	1.8493340	2.7598050	–0.0001470
22	H	2.3332760	–2.2311580	–0.0000270
23	O	4.5363120	–0.9442740	0.0001660
24	H	5.3066930	–0.3433270	0.0002330
25	H	4.0807210	1.7116060	–0.0000190

[a] Absolute energy: E(RCAM–B3LYP) = –630.71718829 a.u.

Table S7. Atom Coordinates of **1c**^{cB} [a]

Tag	Symbol	X	Y	Z
1	C	2.8542970	–2.8637590	0.0000000
2	C	1.6621420	–3.6821370	0.0000000
3	C	0.4445380	–3.0838450	0.0000000
4	N	0.3083440	–1.6903030	0.0000000
5	C	1.4477050	–0.8491230	0.0000000
6	C	2.7381960	–1.5069380	0.0000000
7	C	–0.9528170	–1.1144620	0.0000000
8	C	–1.1483960	0.2382950	0.0000000
9	C	0.0000000	1.1519230	0.0000000
10	C	1.2898630	0.5168020	0.0000000
11	C	–2.4821970	0.8094230	0.0000000
12	C	–2.6569400	2.1544460	0.0000000
13	C	–1.5176400	3.1044240	0.0000000
14	C	–0.1926440	2.5161240	0.0000000
15	H	3.8303080	–3.3362090	0.0000000
16	H	1.7280490	–4.7628550	0.0000000
17	H	–0.4851980	–3.6402050	0.0000000
18	H	3.6128430	–0.8658200	0.0000000
19	H	–1.7865130	–1.8080690	0.0000000
20	H	2.1819090	1.1333920	0.0000000
21	H	–3.3363010	0.1358380	0.0000000
22	H	0.6504940	3.1999120	0.0000000
23	O	–1.7281090	4.3530770	0.0000000
24	H	–3.6457650	2.6044730	0.0000000

[a] Absolute energy : E(RCAM–B3LYP) = –630.30633395 a.u.

Table S8. Atom Coordinates of **1d** [a]

Tag	Symbol	X	Y	Z
1	C	3.7626790	0.9168940	–0.0000010
2	C	3.8811030	–0.5125900	0.0000010
3	C	2.7680870	–1.2945100	0.0000010
4	N	1.4802180	–0.7272190	0.0000010
5	C	1.3332100	0.6712210	–0.0000010
6	C	2.5151480	1.4798150	–0.0000020
7	C	0.3832900	–1.5448340	0.0000020
8	C	–0.9137800	–1.0423550	0.0000010
9	C	–1.0862150	0.3875030	–0.0000010
10	C	0.0433760	1.2087920	–0.0000010
11	C	–2.0605610	–1.9018600	0.0000020
12	C	–3.3152960	–1.3431210	0.0000020
13	C	–3.5045620	0.0763150	0.0000000
14	C	–2.4188940	0.9211530	–0.0000010
15	H	4.6530190	1.5341250	–0.0000020
16	H	4.8552130	–0.9864220	0.0000010
17	H	2.8031830	–2.3763360	0.0000030
18	H	2.3805930	2.5552450	–0.0000030
19	H	0.5766620	–2.6108230	0.0000030
20	H	–0.0814370	2.2846310	–0.0000030
21	H	–4.1925740	–1.9809980	0.0000030
22	H	–4.5150900	0.4744890	0.0000000
23	H	–1.9289190	–2.9785420	0.0000030
24	O	–2.4816180	2.2964900	–0.0000010
25	H	–3.3847430	2.6687080	–0.0000010

[a] Absolute energy: E(RCAM–B3LYP) = –630.71759785 a.u.

Table S9. Atom Coordinates of **1d**^{cB} [a]

Tag	Symbol	X	Y	Z
1	C	3.7572120	0.9016960	–0.0000010
2	C	3.8574300	–0.5271650	0.0000020
3	C	2.7375380	–1.3017840	0.0000040
4	N	1.4483020	–0.7329920	0.0000020
5	C	1.3213030	0.6718440	–0.0000010
6	C	2.5049270	1.4646820	–0.0000030
7	C	0.3494500	–1.5362850	0.0000030
8	C	–0.9642140	–1.0315690	0.0000020
9	C	–1.1092920	0.4184500	–0.0000010
10	C	0.0234380	1.2107670	–0.0000030
11	C	–2.1028760	–1.8524100	0.0000030
12	C	–3.3702590	–1.2349870	0.0000000
13	C	–3.5539630	0.1457290	–0.0000020
14	C	–2.4469350	1.0626760	–0.0000020
15	H	4.6504860	1.5141830	–0.0000030
16	H	4.8259100	–1.0138200	0.0000030
17	H	2.7655250	–2.3838670	0.0000060
18	H	2.3702450	2.5407830	–0.0000060
19	H	0.5378810	–2.6033350	0.0000060
20	H	–0.1152900	2.2874920	–0.0000050
21	H	–4.2533230	–1.8703740	0.0000010
22	H	–4.5512920	0.5731360	–0.0000030
23	H	–2.0072760	–2.9331990	0.0000050
24	O	–2.5479420	2.3337610	–0.0000030

[a] Absolute energy: E(RCAM–B3LYP) = –630.29710182 a.u.

Table S10. Atom Coordinates of **1a(H_2O)$_3$** in the S_0 state [a]

Tag	Symbol	X	Y	Z
1	C	5.1626160	–1.1392590	0.0623880
2	C	4.3123560	–2.2848520	0.0876590
3	C	2.9728790	–2.1359260	0.0692030
4	N	2.3901470	–0.8682910	0.0245480
5	C	3.1915720	0.2729670	–0.0016560
6	C	4.6084400	0.0974000	0.0193320
7	C	1.0404820	–0.7635700	0.0078420
8	C	0.4080220	0.4582570	–0.0350180
9	C	1.1926200	1.6586630	–0.0642670
10	C	2.5817550	1.5155310	–0.0463130
11	C	–1.0311060	0.5373060	–0.0499330
12	C	–1.6256650	1.7742760	–0.0928110
13	C	–0.8331290	2.9492970	–0.1220130
14	C	0.5362290	2.9140460	–0.1088470
15	H	6.2385430	–1.2640330	0.0780090
16	H	4.7267750	–3.2843800	0.1224020
17	H	2.2728520	–2.9594970	0.0880740
18	H	5.2170800	0.9931960	–0.0002570
19	H	0.4845400	–1.6910130	0.0299990
20	H	3.2183640	2.3922990	–0.0674690
21	H	1.1238550	3.8243810	–0.1316060
22	H	–2.7070650	1.8453170	–0.1044660
23	H	–1.3409610	3.9078230	–0.1560120
24	O	–1.6890000	–0.6236320	–0.0198310
25	H	–2.6916160	–0.4981850	–0.0256290
26	O	–4.2440800	–0.3038240	–0.0326720
27	H	–4.7327140	–0.7260790	–0.7713390
28	H	–4.7106150	–0.5219810	0.8024850
29	O	–5.4437750	–0.8288030	2.3870870
30	H	–6.3386060	–0.4957380	2.5341680
31	H	–5.4460400	–1.7428510	2.6997860
32	O	–5.5138530	–1.4248490	–2.2005890
33	H	–6.3278180	–1.0033110	–2.5056300
34	H	–5.6943490	–2.3738490	–2.1896960

[a] Absolute energy: E(RCAM–B3LYP) = –860.20158116 a.u.

Table S11. Atom Coordinates of **1a(H_2O)$_3$** in the S_1 state [a]

Tag	Symbol	X	Y	Z
1	C	5.1940210	–1.0728540	0.0357580
2	C	4.3973270	–2.2324510	0.0519510
3	C	3.0337820	–2.0938450	0.0417480
4	N	2.4336850	–0.8729490	0.0160850
5	C	3.1861550	0.3013470	–0.0015610
6	C	4.5964130	0.1628300	0.0098220
7	C	1.0289210	–0.7992160	0.0075440
8	C	0.3825430	0.4221780	–0.0188380
9	C	1.1256370	1.6360850	–0.0384670
10	C	2.5384610	1.5351000	–0.0289940
11	C	–1.0470360	0.5031570	–0.0268090
12	C	–1.6951390	1.7717080	–0.0544370
13	C	–0.9555860	2.9328870	–0.0734570
14	C	0.4543060	2.8680840	–0.0654680
15	H	6.2751100	–1.1527010	0.0437480
16	H	4.8304080	–3.2235400	0.0723410
17	H	2.3604930	–2.9408250	0.0536730
18	H	5.1883590	1.0699930	–0.0027700
19	H	0.5089490	–1.7440680	0.0232250
20	H	3.1505290	2.4286530	–0.0430490
21	H	1.0336410	3.7849520	–0.0806010
22	H	–2.7789950	1.7903560	–0.0604710
23	H	–1.4520440	3.8954490	–0.0946530
24	O	–1.7213650	–0.6172230	–0.0077780
25	H	–2.7564680	–0.4959550	–0.0120070
26	O	–4.2001490	–0.3213430	–0.0183970
27	H	–4.6773080	–0.7092810	–0.7873320
28	H	–4.6696720	–0.5847850	0.8059910
29	O	–5.4003800	–0.9696520	2.3354680
30	H	–6.2898970	–0.6292020	2.4979140
31	H	–5.4208700	–1.9015920	2.5895450
32	O	–5.4213390	–1.3306150	–2.2294510
33	H	–6.2313600	–0.8965640	–2.5277480
34	H	–5.5996340	–2.2796470	–2.2618830

[a] Absolute energy: E(RCAM–B3LYP) = –860.19145098 a.u.

Table S12. Atom Coordinates of **1b(H_2O)$_3$** in the S_0 state [a]

Tag	Symbol	X	Y	Z
1	C	–5.3538480	–0.9825670	0.0331590
2	C	–4.5855070	–2.1809980	0.0551490
3	C	–3.2366110	–2.1270670	0.0509990
4	C	–4.7094400	0.2122010	0.0075720
5	C	–1.2091510	–0.8987630	0.0225070
6	C	–0.4790650	0.2765440	–0.0028520
7	C	–1.1971790	1.5178090	–0.0275520
8	C	–2.5847130	1.4830260	–0.0240220
9	C	0.9435670	0.2654680	–0.0047610
10	C	1.6264740	1.4545480	–0.0311490
11	C	0.9102420	2.6986820	–0.0567520
12	C	–0.4473270	2.7335560	–0.0548450
13	H	–6.4359180	–1.0307950	0.0369250
14	H	–5.0669450	–3.1506620	0.0757350
15	H	–2.5997130	–3.0003610	0.0673140
16	H	–5.2507620	1.1504050	–0.0099250
17	H	–0.7323310	–1.8699000	0.0414720
18	H	–3.1559500	2.4039440	–0.0422650
19	H	–0.9772360	3.6796400	–0.0739760
20	H	1.4924920	3.6136680	–0.0774420
21	O	4.1009060	–0.7825840	0.0287060
22	H	4.6680010	–0.9623320	0.8083370
23	H	4.6011430	–1.0449910	–0.7729560
24	O	5.3916090	–1.4704960	–2.3085670
25	H	6.2910080	–1.1460230	–2.4468140
26	H	5.4079960	–2.4064590	–2.5470680
27	O	5.5820560	–1.2249110	2.3112630
28	H	6.4037700	–0.7280420	2.4165400
29	H	5.7899940	–2.1363440	2.5545520
30	O	2.9611110	1.5506330	–0.0351050
31	H	1.4806610	–0.6760990	0.0150300
32	H	3.4062140	0.6492980	–0.0108620
33	C	–3.2869740	0.2833080	0.0024280
34	N	–2.5643830	–0.9057980	0.0251080

[a] Absolute energy: E(RCAM–B3LYP) = –860.20172383 a.u.

Table S13. Atom Coordinates of **1b(H$_2$O)$_3$** in the S_1 state [a]

Tag	Symbol	X	Y	Z
1	C	–5.3136870	–0.9974120	–0.0151320
2	C	–4.5708250	–2.1925460	–0.0259440
3	C	–3.2031150	–2.1147120	–0.0245350
4	C	–4.6625770	0.2150960	–0.0032690
5	C	–1.1549020	–0.8945230	–0.0123830
6	C	–0.4445420	0.2990990	–0.0007750
7	C	–1.1419530	1.5519420	0.0113990
8	C	–2.5486550	1.5014010	0.0105910
9	C	0.9609650	0.3064390	–0.0008180
10	C	1.6814320	1.5374730	0.0115570
11	C	0.9911900	2.7598970	0.0235650
12	C	–0.3986230	2.7476950	0.0231860
13	H	–6.3972340	–1.0288070	–0.0161390
14	H	–5.0484810	–3.1628760	–0.0354160
15	H	–2.5659300	–2.9892490	–0.0326430
16	H	–5.2174730	1.1453520	0.0051630
17	H	–0.6723910	–1.8623160	–0.0216680
18	H	–3.1299300	2.4158250	0.0194610
19	H	–0.9368230	3.6905360	0.0323220
20	H	1.5520730	3.6858110	0.0328480
21	O	4.0114800	–0.7713960	–0.0152010
22	H	4.5058720	–1.0435020	0.7899100
23	H	4.5526890	–1.0024530	–0.8028940
24	O	5.4044380	–1.3655450	–2.2887240
25	H	6.3192590	–1.0636290	–2.3621710
26	H	5.4047350	–2.2882380	–2.5750430
27	O	5.2646600	–1.4877480	2.3040150
28	H	6.1144470	–1.0774540	2.5115340
29	H	5.3735830	–2.4312150	2.4813910
30	O	2.9960910	1.5446560	0.0120000
31	H	1.5229970	–0.6214890	–0.0107120
32	H	3.4154200	0.6077740	0.0021220
33	C	–3.2532010	0.2938960	–0.0015400
34	N	–2.5507420	–0.9166100	–0.0128850

[a] Absolute energy: E(RCAM–B3LYP) = –860.19289055 a.u.

Table S14. Atom Coordinates of **1c(H$_2$O)$_3$** in the S_0 state [a]

Tag	Symbol	X	Y	Z
1	C	–5.3708200	–0.8475560	0.0307170
2	C	–4.7191320	–2.1173170	0.0544800
3	C	–3.3647360	–2.1687270	0.0518900
4	C	–4.6423560	0.2859560	0.0054980
5	C	–1.1933840	–0.9834320	0.0226300
6	C	–0.4465990	0.1993480	–0.0029780
7	C	–1.1754350	1.4365130	–0.0275950
8	C	–2.5505050	1.4096090	–0.0241130
9	C	0.9658800	0.2206720	–0.0052980
10	C	1.6323500	1.4265940	–0.0315670
11	C	0.9030910	2.6638330	–0.0571440
12	C	–0.4521530	2.6731750	–0.0551950
13	H	–6.4510360	–0.7758810	0.0325850
14	H	–5.3079170	–3.0264790	0.0745350
15	H	–2.8309960	–3.1111140	0.0696400
16	H	–5.0713070	1.2782630	–0.0133520
17	H	–0.6920470	–1.9440370	0.0414710
18	H	–3.1434640	2.3151240	–0.0419660
19	H	–1.0006170	3.6087410	–0.0744190
20	H	1.4726680	3.5862300	–0.0777850
21	O	4.1402160	–0.7615270	0.0273940
22	H	4.7072240	–0.9323830	0.8095640
23	H	4.6475540	–1.0139170	–0.7734480
24	O	5.4484790	–1.4297990	–2.3015000
25	H	6.3491270	–1.1057640	–2.4326010
26	H	5.4652300	–2.3648600	–2.5435270
27	O	5.6170610	–1.1845930	2.3113990
28	H	6.4364740	–0.6841900	2.4179310
29	H	5.8276980	–2.0946020	2.5577520
30	N	–3.2471390	0.2460670	0.0020480
31	C	–2.5772420	–0.9765830	0.0256150
32	O	2.9595950	1.5359010	–0.0352550
33	H	1.5230260	–0.7090480	0.0141330
34	H	3.4217880	0.6390820	–0.0127850

[a] Absolute energy: E(RCAM–B3LYP) = –860.20443572 a.u.

Table S15. Atom Coordinates of **1c(H$_2$O)$_3$** in the S_1 state [a]

Tag	Symbol	X	Y	Z
1	C	–5.3498710	–0.9018440	0.0204630
2	C	–4.6928310	–2.1315510	0.0331160
3	C	–3.3089850	–2.1603470	0.0304460
4	C	–4.5972110	0.2577780	0.0053190
5	C	–1.1511210	–0.9585340	0.0123160
6	C	–0.4134910	0.2521360	–0.0029750
7	C	–1.1434020	1.4823170	–0.0165010
8	C	–2.5320370	1.4443650	–0.0136180
9	C	0.9762620	0.2762380	–0.0051130
10	C	1.6894170	1.5212730	–0.0214620
11	C	0.9752260	2.7203370	–0.0351080
12	C	–0.4140710	2.6967850	–0.0324410
13	H	–6.4292110	–0.8270480	0.0221290
14	H	–5.2551550	–3.0578310	0.0450880
15	H	–2.7717170	–3.1008690	0.0402120
16	H	–5.0489430	1.2409140	–0.0049950
17	H	–0.6351990	–1.9114940	0.0225880
18	H	–3.1430820	2.3353100	–0.0235680
19	H	–0.9593620	3.6353370	–0.0428900
20	H	1.5172890	3.6582970	–0.0475190
21	O	4.0492590	–0.7716700	0.0157350
22	H	4.5916490	–0.9866710	0.8066480
23	H	4.5556890	–1.0358050	–0.7840760
24	O	5.3471610	–1.4644590	–2.2916080
25	H	6.2512760	–1.1495480	–2.4212820
26	H	5.3552130	–2.4009260	–2.5288500
27	O	5.4515990	–1.3175190	2.3010760
28	H	6.2820250	–0.8447230	2.4431820
29	H	5.6319800	–2.2425910	2.5133330
30	N	–3.2431280	0.2362120	0.0023740
31	C	–2.5491750	–0.9744030	0.0151240
32	O	3.0079790	1.5436800	–0.0239070
33	H	1.5459930	–0.6468650	0.0058490
34	H	3.4332020	0.6134830	–0.0102380

[a] Absolute energy: E(RCAM–B3LYP) = –860.19358547 a.u.

Table S16. Atom Coordinates of **1d(H_2O)$_3$** in the S_0 state [a]

Tag	Symbol	X	Y	Z
1	C	5.1996590	–0.9999540	0.0795700
2	C	4.4671280	–2.2206890	0.1271710
3	C	3.1106990	–2.1773300	0.1081370
4	C	4.5520150	0.1821580	0.0172870
5	C	1.0274080	–0.8451860	0.0186640
6	C	0.3813960	0.3822750	–0.0457420
7	C	1.1721340	1.5757780	–0.0897770
8	C	2.5485000	1.4464780	–0.0652330
9	C	–1.0512230	0.4928000	–0.0689420
10	C	–1.6244760	1.7382800	–0.1337820
11	C	–0.8212320	2.9103140	–0.1779580
12	C	0.5417260	2.8528190	–0.1574210
13	H	6.2823600	–0.9999070	0.0926170
14	H	4.9920600	–3.1668060	0.1780320
15	H	2.5114970	–3.0790760	0.1434150
16	H	5.0504990	1.1406770	–0.0210200
17	H	0.4499460	–1.7600340	0.0524740
18	H	3.2048380	2.3063930	–0.0960470
19	H	1.1484980	3.7501560	–0.1915940
20	H	–2.7053000	1.8228870	–0.1516560
21	H	–1.3185520	3.8730740	–0.2296000
22	O	–1.7354900	–0.6573150	–0.0242900
23	H	–2.7310240	–0.5077920	–0.0348320
24	O	–4.2970250	–0.2777040	–0.0479940
25	H	–4.7952920	–0.7341540	–0.7589010
26	H	–4.7601730	–0.4468480	0.7998860
27	O	–5.4840700	–0.6629450	2.4087380
28	H	–6.3862260	–0.3426410	2.5381480
29	H	–5.4623530	–1.5532930	2.7829840
30	O	–5.5959760	–1.5057110	–2.1445630
31	H	–6.4145560	–1.1007760	–2.4594910
32	H	–5.7745090	–2.4532600	–2.0848630
33	N	3.1584390	0.2393250	–0.0023160
34	C	2.4128840	–0.9368230	0.0416140

[a] Absolute energy: E(RCAM–B3LYP) = –860.19994752 a.u.

Table S17. Atom Coordinates of **1d(H$_2$O)$_3$** of the S1 state [a]

Tag	Symbol	X	Y	Z
1	C	5.2306310	–0.9663640	0.0351610
2	C	4.5131620	–2.1749230	0.0596580
3	C	3.1384540	–2.1487370	0.0531140
4	C	4.5346570	0.2137190	0.0053470
5	C	1.0266190	–0.8605020	0.0138700
6	C	0.3520360	0.3741520	–0.0180830
7	C	1.1281490	1.5682160	–0.0418300
8	C	2.5163150	1.4836190	–0.0323680
9	C	–1.0647570	0.4717990	–0.0272680
10	C	–1.7054170	1.7530160	–0.0609230
11	C	–0.9384380	2.8914130	–0.0839010
12	C	0.4677520	2.8170640	–0.0747220
13	H	6.3122070	–0.9435870	0.0392520
14	H	5.0382920	–3.1228930	0.0836620
15	H	2.5619860	–3.0656930	0.0718170
16	H	5.0217890	1.1797330	–0.0145790
17	H	0.4727950	–1.7893960	0.0325690
18	H	3.1587630	2.3516770	–0.0488740
19	H	1.0519780	3.7307930	–0.0937530
20	H	–2.7881550	1.7915740	–0.0681390
21	H	–1.4159320	3.8642010	–0.1097110
22	O	–1.7623090	–0.6340270	–0.0041870
23	H	–2.7911960	–0.4910580	–0.0105680
24	O	–4.2414970	–0.2955110	–0.0209510
25	H	–4.7203240	–0.6874130	–0.7864240
26	H	–4.7145190	–0.5488080	0.8042380
27	O	–5.4530300	–0.9193490	2.3372050
28	H	–6.3450500	–0.5815190	2.4910660
29	H	–5.4705380	–1.8485010	2.6014990
30	O	–5.4672340	–1.3217530	–2.2253980
31	H	–6.2778680	–0.8909310	–2.5266370
32	H	–5.6447490	–2.2711630	–2.2500660
33	N	3.1717550	0.2477830	–0.0013330
34	C	2.4243050	–0.9302020	0.0220490

[a] Absolute energy: E(RCAM–B3LYP) = –860.18896968 a.u.

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