Supporting Information

Spectroscopic and quantum chemical characterization of the ground and lowest electronically excited singlet and triplet states of halo- and nitro-harmines in aqueous media

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Contents: **Page**

1. Electrostatic potential maps

Figure SI.1. Electrostatic potential maps of neutral species of harmine (**1**), bromoharmines (**5** – **7**) and nitroharmines (**8** – **10**).

2. UV-visible spectroscopic titration of 8 and 10 and pK_a vs Gibbs "acid half-reaction" free energies (ΔG^0) relationship

(a)

(b)

(c)

(Experimental) pK_a = **0.27** (±0.04) ΔG^0 - 57 (±9); (r^2 = 0.75)
(Gibbs isotherm) pK_a = ΔG^0 / RTln10 = **0.733** ΔG^0

1 = Harmine	
2 = 6-chloroharmine	
3 = 8-chloroharmine	
4 = 6,8-dichloroharmine	
5 = 6-bromoharmine	
6 = 8-bromoharmine	
7 = 6,8-dibromoharmine	
8 = 6-nitroharmine	
9 = 8-nitroharmine	
10 = 6,8-dinitroharmine	
11 = 9-methylharmine	
12 = Harmalane	
13 = 6-methoxyharmalane	
14 = 6-methoxyharmane	
15 = Harmalina	
16 = Harmol	
17 = Harmalol	
18 = Harmane	

(d)
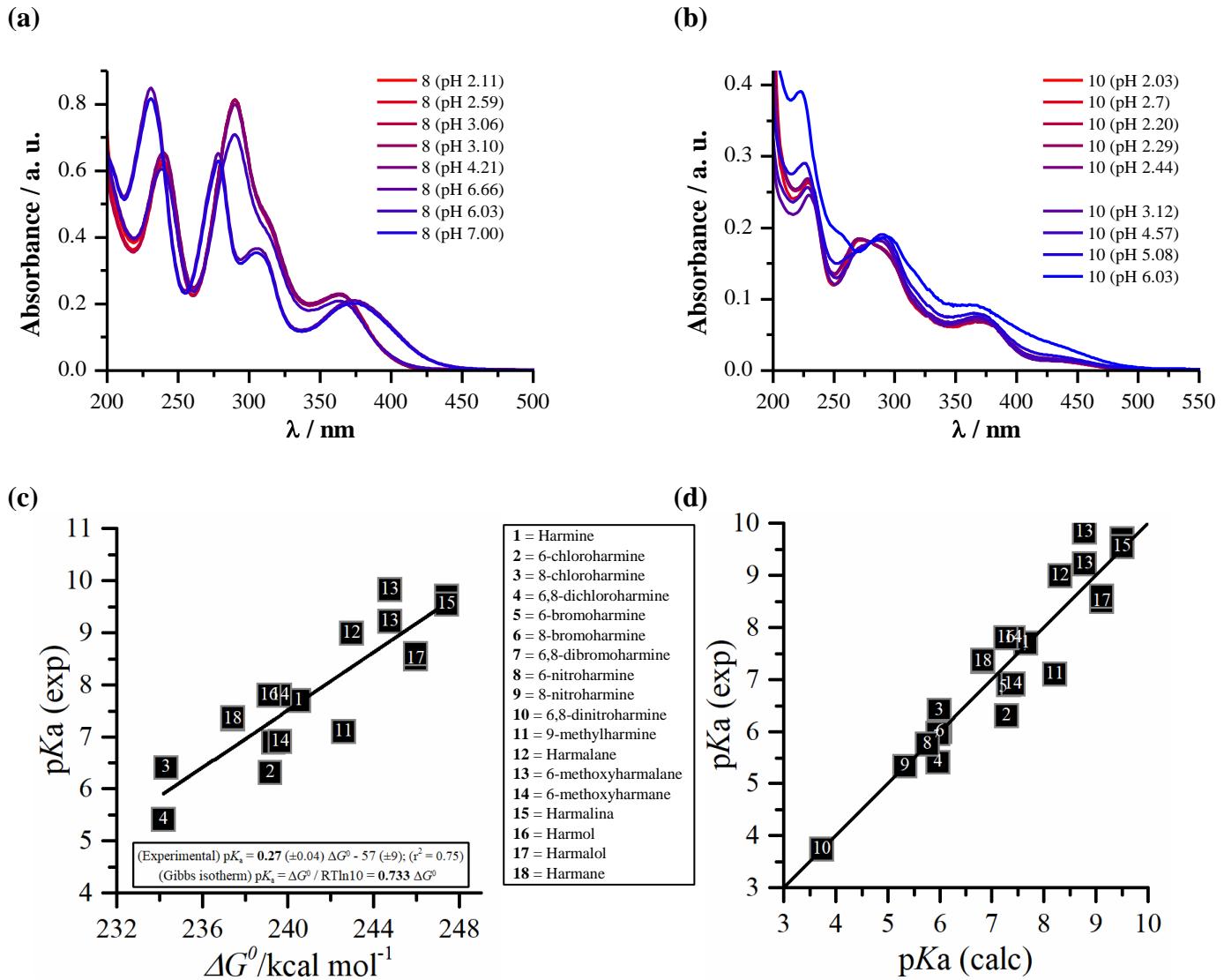
Figure SI.2. (a) and **(b)** UV-visible absorption spectra pH-evolution of 6-nitroharmine (**8**) and 6,8-dinitroharmine (**10**), respectively. **(c)** Relationship between the experimental pK_a and the difference between Gibbs "acid half-reaction" free energies (ΔG^0) between cationic (**C**) and neutral (**N**) species in the gas phase. **(d)** Relationship between the experimental and calculated pK_a values.

4

3. UV-visible experimental and theoretical spectra of C and N species of 5 – 7

(a)

(b)

(c)

(d)

(e)

(f)
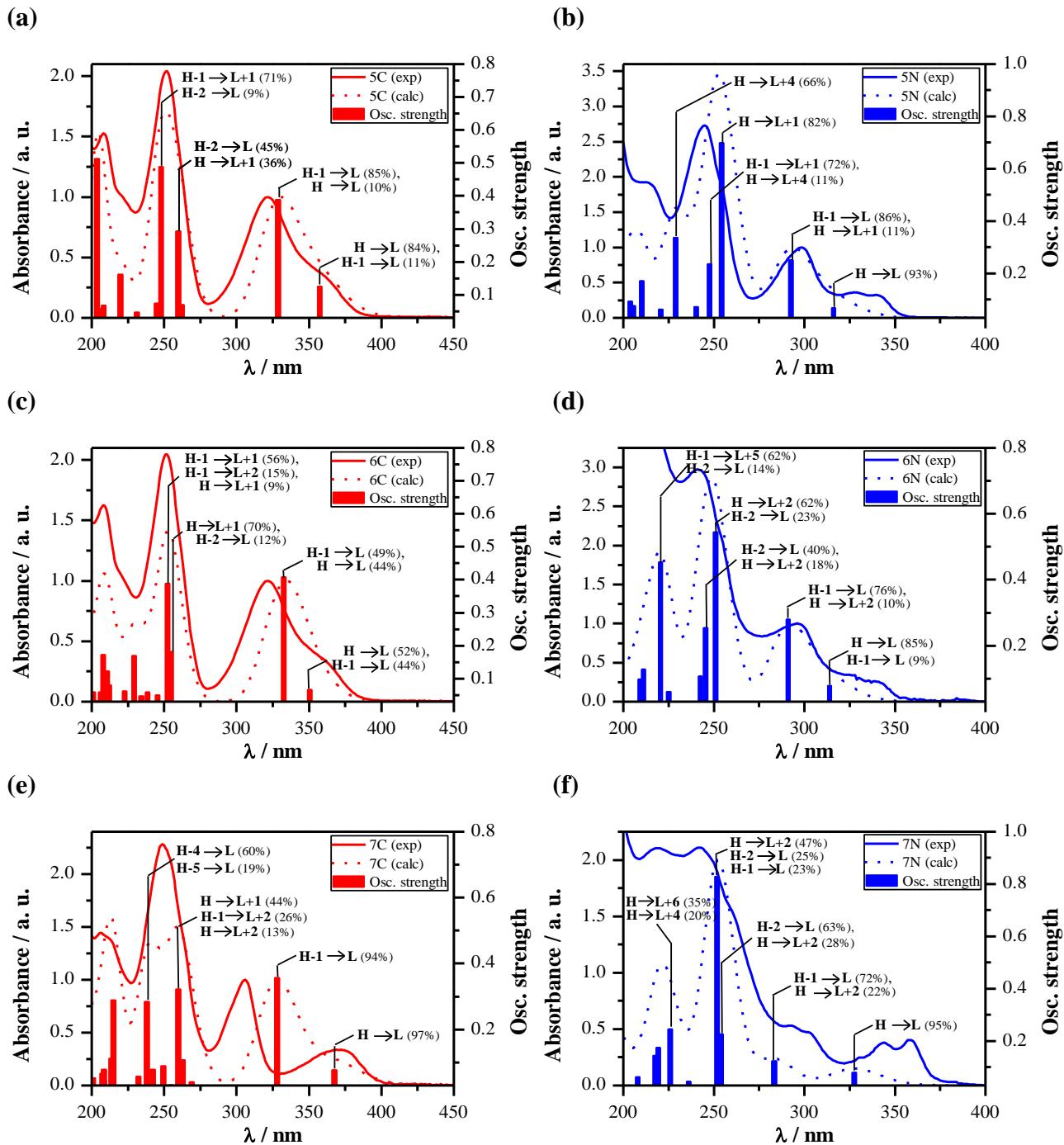
Figure SI.3. Experimental (solid lines) and calculated (dashed lines) absorption spectra of cationic (**C**) (red) and neutral (**N**) (blue) species of compounds **5** (a, b), **6** (c, d) and **7** (e, f).

4.   UV-visible experimental and theoretical spectra of C and N species of 8 – 10

(a)

(b)

(c)

(d)

(e)

(f)
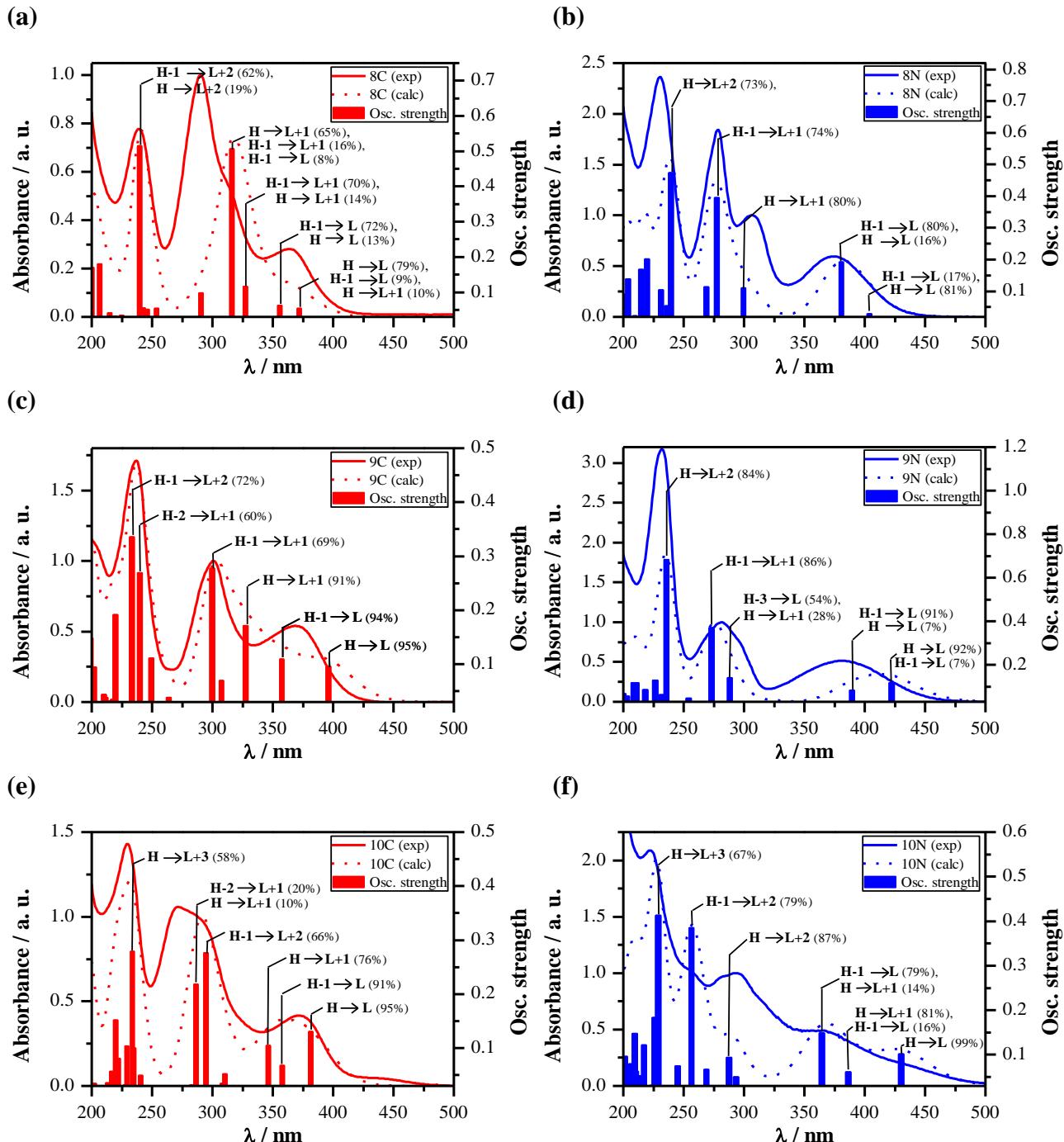
Figure SI.4. Experimental (solid lines) and calculated (dashed lines) absorption spectra of cationic (**C**) (red) and neutral (**N**) (blue) species of compounds **8** (a, b), **9** (c, d) and **10** (e, f).

5. UV-visible experimental and theoretical spectra of Z species of 5 – 10

(a)

(b)

(c)

(d)

(e)

(f)
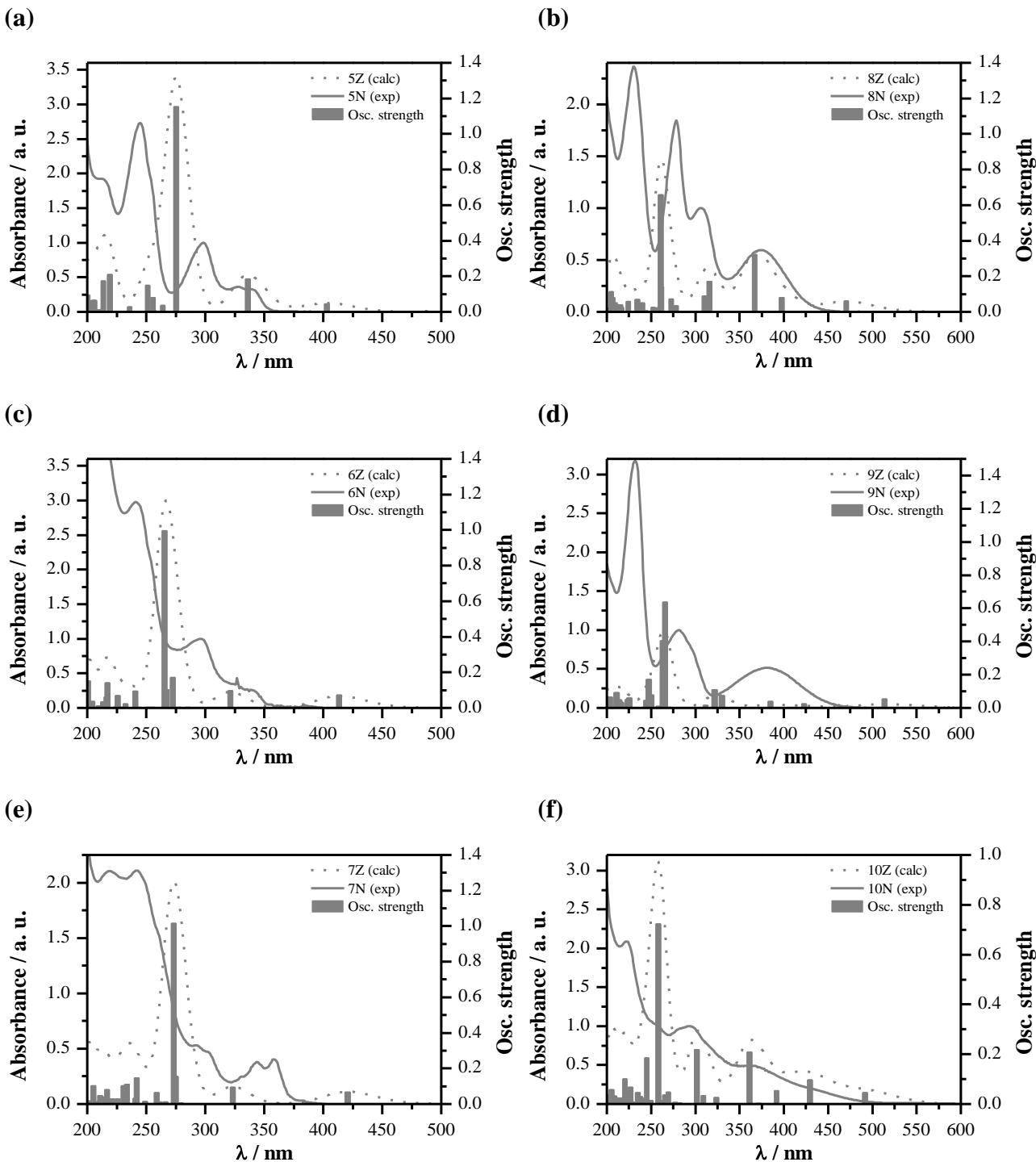
Figure SI.5. Experimental (solid lines) and calculated (dashed lines) absorption spectra of neutral (**N**) and zwitterionic (**Z**) species of **(a)** 6-bromoharmine (**5**), **(b)** 6-nitroharmine (**8**), **(c)** 8-bromoharmine (**6**), **(d)** 8-nitroharmine (**9**), **(e)** 6,8-dibromoharmine (**7**) and **(f)** 6,8-dinitroharmine (**10**).

Table SI.1. Theoretical data of the 50 electronic transitions calculated for the cationic species of 6-bromoharmine (**5C**).

| No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribution)
1	27980.98625	357.39	0.1259	H-1->LUMO (11%), **HOMO->LUMO (84%)**, H-1->L+1 (3%)
2	30420.00684	328.73	0.3888	**H-1->LUMO (85%)**, HOMO->LUMO (10%), HOMO->L+1 (3%)
3	38135.50651	262.22	0.0694	H-2->LUMO (29%), H-1->L+1 (10%), HOMO->L+1 (56%)
4	38497.64945	259.76	0.2939	**H-2->LUMO (45%), HOMO->L+1 (36%)**, H-1->L+1 (6%), H-1->L+2 (5%), HOMO->L+2 (2%)
5	40347.07876	247.85	0.4878	**H-1->L+1 (71%)**, H-4->LUMO (2%), H-2->LUMO (9%), H-1->L+2 (4%), HOMO->LUMO (4%), HOMO->L+2 (4%)
6	40359.17707	247.78	0.0008	HOMO->L+3 (96%)
7	40850.36872	244.80	0.0744	HOMO->L+2 (78%) H-2->LUMO (8%), H-1->L+1 (4%), H-1->L+7 (4%)
8	41034.26313	243.70	0.0001	H-3->LUMO (98%)
9	43238.57638	231.27	0.0465	H-1->L+2 (81%) H-2->LUMO (6%), HOMO->L+2 (5%), HOMO->L+7 (2%)
10	43306.32696	230.91	0.0001	H-1->L+3 (97%)
11	44370.9788	225.37	0.0001	HOMO->L+4 (88%) HOMO->L+5 (5%)
12	45323.51958	220.64	0.0005	H-1->L+4 (88%) H-1->L+5 (5%), HOMO->L+5 (2%)
13	45501.76811	219.77	0.161	**H-4->LUMO (83%)**, H-2->L+1 (7%)
14	46903.55971	213.20	0.0032	HOMO->L+5 (76%) HOMO->L+4 (8%), HOMO->L+6 (9%)
15	47518.15418	210.45	0.0013	HOMO->L+5 (13%), HOMO->L+6 (80%) H-1->L+6 (2%)
16	47981.11643	208.42	0.0102	H-1->L+5 (90%) H-1->L+4 (5%)
17	48014.99171	208.27	0.0683	H-5->LUMO (60%), HOMO->L+7 (27%) H-2->L+1 (5%), H-1->L+7 (4%)
18	48482.79328	206.26	0.0571	H-5->LUMO (18%), H-2->L+1 (13%), HOMO->L+7 (53%) H-2->L+2 (6%), H-1->L+2 (3%)
19	48905.4278	204.48	0	H-1->L+6 (92%)
20	49100.61397	203.66	0.5126	**H-2->L+1 (31%), H-1->L+7 (61%)**, HOMO->L+7 (2%)
21	50118.48566	199.53	0.0002	HOMO->L+8 (92%), HOMO->L+6 (3%)
22	51170.23264	195.43	0.0012	H-1->L+8 (93%)
23	51372.6778	194.66	0.0002	H-3->L+1 (72%), H-3->L+2 (24%)
24	51590.4475	193.83	0.0129	H-6->LUMO (33%), H-3->L+3 (13%), H-2->L+2 (46%) HOMO->L+7 (3%)
25	51697.71924	193.43	0.0093	HOMO->L+9 (87%) HOMO->L+6 (2%)
26	52080.02604	192.01	0.014	H-3->L+3 (84%) H-6->LUMO (6%), H-2->L+2 (7%)
27	52128.4193	191.83	0.0004	H-7->LUMO (94%) H-8->LUMO (2%)
28	52452.65418	190.65	0.017	H-5->LUMO (11%), H-2->L+1 (22%), H-1->L+7 (12%), HOMO->L+10 (27%) H-6->LUMO (9%), H-4->LUMO (3%), H-4->L+2 (2%), HOMO->L+2 (2%), HOMO->L+7 (4%)
29	52804.31191	189.38	0.0017	H-2->L+3 (24%), HOMO->L+11 (61%) HOMO->L+12 (6%)
30	52958.36381	188.83	0.0006	H-2->L+3 (27%), H-1->L+9 (55%) HOMO->L+11 (7%)
31	53017.24228	188.62	0.0793	H-6->LUMO (27%), H-2->L+2 (13%), H-1->L+10 (11%), HOMO->L+10 (42%)
32	53154.35653	188.13	0.0671	H-2->L+1 (11%), H-2->L+2 (13%), H-1->L+10 (11%), HOMO->L+10 (27%) H-6->LUMO (9%), H-4->LUMO (2%), H-4->L+1 (7%), H-4->L+2 (3%), H-1->L+7 (9%)
33	53285.01835	187.67	0.0001	H-2->L+3 (37%), H-1->L+9 (37%), HOMO->L+11 (19%)
34	54139.96605	184.71	0.0003	H-3->L+1 (25%), H-3->L+2 (74%)
35	54227.88048	184.41	0.0673	H-1->L+10 (72%) H-6->LUMO (8%), H-4->L+1 (2%), H-2->L+2 (9%)
36	54261.75577	184.29	0.0023	H-1->L+11 (64%), HOMO->L+12 (16%) H-1->L+12 (5%), HOMO->L+14 (3%)
37	54565.82679	183.26	0.0076	H-1->L+11 (22%), HOMO->L+12 (61%) H-2->L+4 (4%), HOMO->L+11 (3%), HOMO->L+14 (3%)
38	55120.73623	181.42	0.0045	H-2->L+4 (78%) H-1->L+12 (8%), HOMO->L+12 (6%)
39	55602.24923	179.85	0.0001	HOMO->L+14 (79%) H-1->L+12 (6%), HOMO->L+12 (6%)
40	55628.05897	179.77	0	H-1->L+12 (64%) H-2->L+4 (9%), H-1->L+11 (3%), H-1->L+14 (9%), HOMO->L+14 (7%)
41	55728.07172	179.44	0.0011	HOMO->L+13 (95%) H-1->L+10 (2%)
42	56599.95706	176.68	0.0053	H-4->L+1 (17%), H-1->L+13 (74%) H-2->L+7 (3%)
43	56713.68123	176.32	0.003	H-9->LUMO (28%), H-8->LUMO (29%), HOMO->L+15 (34%) H-11->LUMO (2%)
44	56732.23198	176.27	0.0027	H-9->LUMO (18%), H-8->LUMO (17%), H-1->L+14 (10%), HOMO->L+15 (47%)
45	56834.66439	175.95	0	H-1->L+12 (11%), H-1->L+14 (72%) HOMO->L+15 (6%)
46	56888.70354	175.78	0.0624	H-4->L+1 (57%), H-1->L+13 (22%) H-2->L+7 (9%)
47	57678.32033	173.38	0.0003	H-9->LUMO (51%), H-8->LUMO (44%)
48	57822.69357	172.94	0.0011	H-2->L+5 (85%) H-2->L+6 (3%), H-2->L+8 (2%), H-1->L+15 (2%)
49	57889.63759	172.74	0.0009	H-1->L+15 (88%) H-2->L+5 (3%)
50	58084.0172	172.16	0.1116	H-4->L+2 (10%), H-2->L+7 (69%) H-5->L+1 (7%), H-4->L+1 (7%)

Table SI.2. Theoretical data of the 50 electronic transitions calculated for the cationic species of 8-bromoharmine (**6C**).

No.	Energy (cm^{-1})	λ (nm)	Osc.	Symmetry (% contribs)
1	28539.12192	350.40	0.0663	**H-1->LUMO (44%), HOMO->LUMO (52%)**
2	30077.22121	332.48	0.4089	**H-1->LUMO (49%), HOMO->LUMO (44%)** H-1->L+1 (3%), HOMO->L+1 (3%)
3	37974.19563	263.34	0.016	H-2->LUMO (59%), H-1->L+1 (11%), HOMO->L+2 (24%) HOMO->L+1 (3%)
4	38184.70633	261.88	0.0115	HOMO->L+1 (10%), HOMO->L+2 (59%), HOMO->L+3 (11%) H-2->LUMO (9%), H-1->L+1 (7%)
5	39248.55162	254.79	0.1809	H-2->LUMO (12%), **HOMO->L+1 (70%)** H-1->LUMO (3%), HOMO->L+2 (3%), HOMO->L+3 (3%)
6	39619.56666	252.40	0.3886	**H-1->L+1 (56%)**, H-1->L+2 (15%) H-3->LUMO (3%), H-2->LUMO (5%), HOMO->L+1 (9%), HOMO->L+3 (4%)
7	40739.06421	245.46	0.0504	H-1->L+1 (11%), H-1->L+2 (77%) H-3->LUMO (3%), H-2->LUMO (4%), H-1->L+3 (2%)
8	41908.56813	238.61	0.059	H-3->LUMO (91%) H-1->L+1 (3%)
9	42696.57181	234.21	0.0473	H-1->L+3 (53%), HOMO->L+3 (21%) H-2->LUMO (5%), H-1->L+1 (3%), HOMO->L+2 (2%), HOMO->L+5 (6%), HOMO->L+6
10	43606.3652	229.32	0.1696	H-4->LUMO (10%), **H-1->L+3 (25%)**, **HOMO->L+3 (50%)** HOMO->L+2 (6%), HOMO->L+5 (2%)
11	44910.56372	222.66	0.0611	H-4->LUMO (34%), HOMO->L+4 (49%) HOMO->L+3 (4%), HOMO->L+5 (3%), HOMO->L+6 (3%)
12	45088.81224	221.78	0.0148	H-4->LUMO (42%), HOMO->L+4 (32%), H-2->L+1 (6%), H-1->L+4 (4%), HOMO->L+2 (2%), HOMO->L+3 (2%), HOMO->L
13	46001.83186	217.38	0.0107	H-1->L+4 (81%) H-1->L+6 (5%), HOMO->L+5 (5%)
14	47135.84739	212.15	0.0798	H-5->LUMO (67%), HOMO->L+5 (19%) H-2->L+1 (4%), H-1->L+4 (2%)
15	47477.82646	210.62	0.1227	H-5->LUMO (25%), **HOMO->L+5 (52%)** H-2->L+1 (6%), H-1->L+4 (3%), HOMO->L+4 (5%), HOMO->L+6 (4%)
16	48073.06363	208.02	0.1715	H-2->L+1 (12%), **HOMO->L+6 (65%)** H-5->LUMO (4%), H-1->L+5 (5%), H-1->L+6 (2%), HOMO->L+4 (5%)
17	48498.92437	206.19	0.0586	H-1->L+5 (62%), H-1->L+6 (18%) H-2->L+1 (2%), H-1->L+4 (3%), HOMO->L+6 (5%), HOMO->L+7 (3%)
18	48760.24801	205.09	0.009	HOMO->L+7 (74%) H-2->L+2 (6%), H-1->L+5 (5%), H-1->L+7 (7%)
19	49324.83611	202.74	0.0312	H-2->L+2 (18%), H-1->L+6 (52%), HOMO->L+7 (10%) H-1->L+4 (2%), H-1->L+5 (8%)
20	49611.16293	201.57	0.0029	H-1->L+7 (84%) H-2->L+2 (6%), HOMO->L+7 (4%)
21	49789.41146	200.85	0.0592	H-2->L+2 (53%), H-1->L+6 (14%) H-4->L+2 (3%), H-2->L+3 (5%), H-1->L+5 (9%), H-1->L+7 (3%), HOMO->L+3 (
22	50484.66137	198.08	0.0578	H-6->LUMO (15%), H-2->L+1 (42%) H-7->LUMO (5%), H-4->LUMO (3%), H-3->L+2 (8%), H-1->L+3 (3%), HOMO->L+5
23	51069.41334	195.81	0.0011	H-3->L+2 (25%), HOMO->L+8 (63%) H-3->L+1 (2%)
24	51283.95681	194.99	0.0072	H-6->LUMO (16%), H-3->L+2 (40%), HOMO->L+8 (23%) H-3->L+1 (4%), H-3->L+3 (2%), H-2->L+1 (2%), H-2->L+3
25	51980.81984	192.38	0.0241	H-7->LUMO (13%), H-6->LUMO (26%), H-1->L+8 (33%) H-3->L+1 (2%), H-3->L+2 (4%), H-3->L+3 (4%), H-2->L+1
26	52122.77342	191.85	0.0144	H-6->LUMO (18%), H-1->L+8 (53%) H-7->LUMO (9%), HOMO->L+9 (5%)
27	52400.22814	190.84	0.0014	HOMO->L+9 (84%) H-1->L+8 (4%), HOMO->L+10 (3%)
28	52741.40067	189.60	0.0903	H-3->L+1 (25%), H-2->L+3 (56%) H-7->LUMO (3%), H-4->L+1 (3%), H-3->L+3 (3%), H-2->L+2 (2%)
29	53009.17674	188.65	0.0928	H-3->L+1 (46%), H-2->L+3 (17%), HOMO->L+10 (10%) H-7->LUMO (3%), H-6->LUMO (3%), H-4->L+1 (5%), H-3->L
30	53126.93368	188.23	0.0139	H-1->L+9 (51%), HOMO->L+10 (21%), HOMO->L+11 (11%) H-3->L+1 (4%)
31	53273.72659	187.71	0.0153	H-1->L+9 (33%), HOMO->L+10 (53%) H-6->LUMO (2%)
32	53606.02701	186.55	0.0109	HOMO->L+11 (72%) H-1->L+9 (4%), HOMO->L+10 (6%), HOMO->L+15 (3%)
33	54231.1067	184.40	0.0157	H-7->LUMO (27%), H-1->L+10 (32%) H-8->LUMO (3%), H-6->LUMO (4%), H-4->L+1 (4%), H-2->L+1 (4%), H-1->L+
34	54295.63105	184.18	0.0298	H-7->LUMO (19%), H-1->L+10 (45%) H-6->LUMO (8%), H-4->L+1 (4%), H-2->L+1 (4%), H-1->L+11 (4%)
35	54509.36798	183.45	0.0055	H-1->L+10 (13%), H-1->L+11 (44%), HOMO->L+12 (14%) H-2->L+4 (8%), H-1->L+12 (4%), HOMO->L+14 (5%)
36	54697.29516	182.82	0.003	H-2->L+4 (45%), H-1->L+11 (24%), HOMO->L+12 (10%) HOMO->L+13 (3%)
37	55207.84411	181.13	0.0074	H-2->L+4 (32%), HOMO->L+12 (51%) H-1->L+11 (6%)
38	55392.54507	180.53	0.0028	H-8->LUMO (43%), H-3->L+3 (30%) H-10->LUMO (3%), H-9->LUMO (6%), H-4->L+1 (3%), H-3->L+1 (4%), H-3->L+
39	55522.40034	180.11	0.0205	H-8->LUMO (28%), H-3->L+3 (42%) H-4->L+1 (8%), H-3->L+1 (4%), H-3->L+2 (7%)
40	55831.31068	179.11	0.0402	H-4->L+1 (14%), H-1->L+12 (10%), HOMO->L+13 (50%) H-8->LUMO (2%), H-7->LUMO (2%), H-4->L+2 (8%)
41	55905.51369	178.87	0.0352	H-4->L+1 (18%), H-1->L+12 (10%), HOMO->L+13 (29%) H-8->LUMO (5%), H-7->LUMO (4%), H-2->L+3 (3%), H-2->
42	56011.97888	178.53	0.0161	H-1->L+12 (23%), HOMO->L+14 (27%) H-8->LUMO (2%), H-7->LUMO (3%), H-4->L+1 (9%), H-4->L+2 (7%), H-1->L
43	56153.93246	178.08	0.0105	H-1->L+12 (34%), HOMO->L+14 (49%) H-1->L+14 (3%), HOMO->L+13 (3%)
44	56489.4591	177.02	0.0262	H-4->L+2 (55%) H-10->LUMO (3%), H-9->LUMO (6%), H-2->L+5 (7%), H-2->L+6 (2%), H-1->L+13 (3%), HOMO->L+
45	56641.09133	176.55	0.0032	H-10->LUMO (46%), H-9->LUMO (31%) H-8->LUMO (9%), H-4->L+2 (4%), H-2->L+5 (3%)
46	56827.4054	175.97	0.0086	H-1->L+13 (73%) H-4->L+2 (5%), H-2->L+5 (4%), H-1->L+12 (2%), H-1->L+14 (8%)
47	56997.58839	175.45	0.1342	H-4->L+1 (14%), H-2->L+5 (55%) H-5->L+1 (2%), H-4->L+2 (4%), H-2->L+6 (5%), H-1->L+13 (3%), H-1->L+14
48	57357.31166	174.35	0.0039	H-1->L+13 (13%), H-1->L+14 (72%) H-2->L+5 (3%), H-1->L+12 (4%)
49	57432.32123	174.12	0.0032	HOMO->L+15 (81%) H-5->L+2 (3%), HOMO->L+11 (4%)
50	57661.38268	173.43	0.0094	H-5->L+1 (14%), H-5->L+2 (58%) H-2->L+6 (5%), H-2->L+7 (2%), HOMO->L+15 (4%)

Table SI.3. Theoretical data of the 50 electronic transitions calculated for the cationic species of 6,8-dibromoharmine (**7C**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	27208.30711	367.53	0.0775	**HOMO->LUMO (97%)**
2	30490.98363	327.97	0.3565	**H-1->LUMO (94%)** HOMO->L+1 (4%)
3	36839.37354	271.45	0.0188	HOMO->L+1 (13%), HOMO->L+2 (77%) H-2->LUMO (2%), H-1->L+2 (2%), HOMO->L+3 (2%)
4	37157.15599	269.13	0.0399	H-2->LUMO (87%) H-1->L+1 (2%), H-1->L+2 (2%), H-1->L+3 (3%)
5	38041.9462	262.87	0.1065	H-1->L+1 (14%), H-1->L+2 (51%), HOMO->L+1 (26%)
6	38495.22979	259.77	0.3217	**H-1->L+2 (26%), HOMO->L+1 (44%)**, HOMO->L+2 (13%) H-4->LUMO (4%), H-3->LUMO (2%), H-1->LUMO (3%), H-1->L+1 (3%)
7	39283.23346	254.56	0.0318	H-3->LUMO (94%) HOMO->L+1 (3%)
8	40084.14201	249.48	0.089	H-1->L+1 (62%), H-1->L+2 (12%) H-2->LUMO (2%), H-1->L+3 (7%), HOMO->L+3 (5%), HOMO->L+4 (4%), HOMO->L+5 (3%)
9	41301.23265	242.12	0.0786	H-5->LUMO (29%), HOMO->L+3 (46%) H-1->L+1 (8%), H-1->L+3 (7%)
10	41355.27179	241.81	0.0451	H-5->LUMO (47%), H-4->LUMO (29%), HOMO->L+3 (13%) H-1->L+1 (4%), H-1->L+3 (3%)
11	42002.935	238.08	0.2847	H-5->LUMO (19%), **H-4->LUMO (60%)** H-2->L+1 (4%), HOMO->L+1 (6%), HOMO->L+3 (5%)
12	43065.16718	232.21	0.057	H-1->L+3 (58%), HOMO->L+3 (20%) H-2->LUMO (4%), H-1->L+2 (3%), HOMO->L+4 (5%), HOMO->L+5 (3%)
13	44342.7494	225.52	0.003	HOMO->L+4 (13%), HOMO->L+5 (33%), HOMO->L+6 (42%) HOMO->L+8 (2%)
14	44829.90827	223.07	0.0016	H-6->LUMO (93%) H-2->L+1 (2%)
15	45280.7722	220.84	0.0282	HOMO->L+4 (47%), HOMO->L+6 (29%) H-1->L+3 (2%), HOMO->L+5 (6%), HOMO->L+7 (9%)
16	46505.12182	215.03	0.2882	**HOMO->L+4 (18%), HOMO->L+5 (41%)** H-2->L+1 (3%), H-1->L+3 (8%), H-1->L+5 (4%), H-1->L+6 (5%), HOMO->L+6 (9%)
17	46580.93794	214.68	0.0204	H-1->L+5 (33%), H-1->L+6 (46%) H-2->L+2 (2%), H-1->L+8 (2%), HOMO->L+6 (5%)
18	46821.29116	213.58	0.1123	H-7->LUMO (11%), H-1->L+4 (74%) H-2->L+1 (3%), H-1->L+7 (5%)
19	47459.27571	210.71	0.0171	H-7->LUMO (52%) H-2->L+1 (7%), H-2->L+2 (8%), H-1->L+5 (9%), H-1->L+6 (7%), H-1->L+7 (4%), HOMO->L+8 (2%)
20	47976.2771	208.44	0.0462	H-2->L+1 (20%), H-2->L+2 (34%), H-1->L+6 (19%) H-1->L+5 (9%), H-1->L+7 (4%), HOMO->L+7 (6%)
21	48009.34583	208.29	0.0781	HOMO->L+7 (66%) H-2->L+1 (5%), H-1->L+5 (8%), H-1->L+6 (3%), HOMO->L+4 (2%), HOMO->L+5 (4%), HOMO->L+6 (4%)
22	48231.95485	207.33	0.0657	H-7->LUMO (15%), H-2->L+2 (38%), H-1->L+5 (11%), HOMO->L+7 (11%), H-2->L+1 (5%), H-2->L+3 (2%), H-1->L+4 (4%), HOMO->L+8 (3%)
23	48698.94987	205.34	0.0105	HOMO->L+8 (83%) H-1->L+5 (4%), HOMO->L+6 (3%)
24	48907.84747	204.47	0.0026	H-3->L+1 (22%), H-3->L+2 (66%) H-3->L+5 (3%), H-3->L+6 (4%)
25	49753.11651	200.99	0.0531	H-2->L+1 (24%), H-1->L+5 (15%), H-1->L+7 (24%) H-8->LUMO (5%), H-7->LUMO (5%), H-2->L+2 (3%), H-1->L+6 (8%)
26	50105.58079	199.58	0.0027	H-3->L+1 (53%), H-3->L+2 (12%), H-3->L+3 (17%) H-5->L+2 (6%), H-3->L+4 (3%)
27	50198.33455	199.21	0.0148	H-5->L+2 (28%), H-1->L+7 (32%), H-8->LUMO (2%), H-5->L+1 (5%), H-4->L+2 (2%), H-3->L+1 (4%), H-3->L+2 (2%), H-3->L+3 (2%), H-2->L+1 (3%), H-1->L+4 (5%)
28	50412.07148	198.37	0.0187	H-5->L+2 (28%), H-4->L+2 (12%), H-1->L+7 (20%), H-8->LUMO (4%), H-7->LUMO (4%), H-5->L+1 (5%), H-4->L+1 (2%), H-2->L+1 (8%), H-1->L+4 (4%)
29	50950.84983	196.27	0.1316	H-2->L+3 (81%) H-8->LUMO (3%), H-4->L+1 (4%), HOMO->L+9 (2%)
30	51004.88898	196.06	0.0003	H-1->L+8 (87%) H-1->L+6 (4%)
31	51545.28045	194.00	0.0028	H-4->L+1 (14%), H-4->L+2 (36%), HOMO->L+9 (24%) H-8->LUMO (2%), H-5->L+2 (7%), H-1->L+8 (2%)
32	51641.26043	193.64	0.0074	H-4->L+2 (15%), HOMO->L+9 (66%) H-8->LUMO (2%), H-5->L+2 (5%)
33	52452.65418	190.65	0.0007	H-5->L+1 (56%), H-5->L+3 (17%), H-4->L+1 (11%) H-5->L+2 (6%), H-4->L+2 (4%), H-4->L+3 (4%)
34	52647.0338	189.94	0.0015	H-8->LUMO (13%), H-4->L+1 (29%), HOMO->L+10 (19%) H-9->LUMO (9%), H-5->L+1 (4%), H-4->L+2 (7%), H-4->L+3 (6%)
35	52822.05611	189.31	0.0085	HOMO->L+10 (69%) H-8->LUMO (5%), H-4->L+1 (6%), H-4->L+2 (3%)
36	53068.05521	188.44	0.0002	H-3->L+1 (13%), H-3->L+3 (73%) H-3->L+2 (9%)
37	53280.17903	187.69	0.0076	H-1->L+9 (83%) H-9->LUMO (4%), H-8->LUMO (4%)
38	53524.56502	186.83	0.0075	HOMO->L+11 (82%) H-9->LUMO (4%), H-8->LUMO (3%)
39	53864.93099	185.65	0.0777	H-8->LUMO (34%), H-4->L+1 (12%), H-4->L+3 (13%) H-9->LUMO (3%), H-6->L+2 (5%), H-5->L+1 (3%), H-4->L+2 (2%), H-2->L+1 (2%), H-2->L+3 (2%), H-1->L+9 (6%), HOMO->L+11 (3%)
40	54040.75985	185.05	0.0115	H-9->LUMO (38%), HOMO->L+12 (31%) H-6->L+1 (2%), H-6->L+2 (6%), H-4->L+1 (3%), HOMO->L+11 (4%)
41	54119.80219	184.78	0.0062	H-6->L+2 (22%), HOMO->L+12 (47%) H-9->LUMO (5%), H-6->L+1 (5%), H-5->L+2 (2%), HOMO->L+11 (4%)
42	54272.24097	184.26	0.1212	H-9->LUMO (19%), H-6->L+2 (31%) H-8->LUMO (3%), H-6->L+1 (3%), H-5->L+1 (2%), H-4->L+1 (4%), H-3->L+6 (2%), H-2->L+3 (3%), H-2->L+4 (5%), HOMO->L+12 (8%), HOMO->L+13 (4%)
43	54584.37754	183.20	0.0426	H-2->L+4 (55%), H-2->L+5 (16%) H-1->L+10 (6%), HOMO->L+13 (4%), HOMO->L+14 (3%)
44	54835.21596	182.36	0.0101	H-1->L+10 (68%), H-1->L+11 (14%) H-2->L+4 (5%), H-1->L+13 (3%)
45	54866.67159	182.26	0.0562	H-2->L+4 (24%), H-2->L+5 (38%), HOMO->L+13 (23%)
46	55042.50045	181.68	0.0006	H-5->L+1 (13%), H-5->L+3 (64%) H-9->LUMO (2%), H-5->L+2 (5%), H-4->L+3 (7%)
47	55319.95518	180.77	0.0377	H-2->L+5 (31%), HOMO->L+13 (47%) HOMO->L+12 (4%), HOMO->L+14 (4%)
48	55437.71212	180.38	0.0034	H-1->L+10 (14%), H-1->L+11 (63%) H-1->L+12 (7%), HOMO->L+13 (3%)
49	55645.80317	179.71	0.0366	H-10->LUMO (11%), H-6->L+1 (33%), H-6->L+3 (11%), H-4->L+3 (17%), H-11->LUMO (4%), H-8->LUMO (2%), H-6->L+2 (3%), H-1->L+11 (2%)
50	55858.73353	179.02	0.0237	H-10->LUMO (62%) H-11->LUMO (8%), H-6->L+1 (9%), H-3->L+4 (2%)

Table SI.4. Theoretical data of the 50 electronic transitions calculated for the cationic species of 6-nitroharmine (**8C**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	26890.52466	371.88	0.0535	**HOMO->LUMO (79%)**, HOMO->L+1 (10%) H-1->LUMO (9%)
2	28109.22841	355.76	0.0627	**H-1->LUMO (72%)**, HOMO->LUMO (13%) H-2->LUMO (3%), H-1->L+1 (5%), HOMO->L+1 (3%)
3	30537.76379	327.46	0.1159	**H-1->L+1 (70%)**, HOMO->L+1 (14%) HOMO->LUMO (4%), HOMO->L+2 (2%)
4	31637.90403	316.08	0.5066	H-1->L+1 (16%), **HOMO->L+1 (65%)** H-1->LUMO (8%), H-1->L+2 (3%), HOMO->LUMO (3%)
5	34437.45446	290.38	0.0983	**H-3->LUMO (34%)**, H-3->L+1 (11%), **H-2->LUMO (27%)** H-4->LUMO (3%), H-2->L+1 (5%), H-1->LUMO (7%), H-1->L+1 (4%), HOMO->L+1 (4%)
6	36233.65117	275.99	0.0074	H-5->LUMO (18%), H-4->LUMO (28%), H-3->LUMO (21%) H-5->L+1 (5%), H-4->L+1 (9%), H-3->L+1 (6%), H-2->LUMO (5%)
7	39415.50839	253.71	0.0546	H-2->LUMO (38%), H-2->L+1 (18%), HOMO->L+2 (21%) H-4->LUMO (6%), H-3->LUMO (5%), H-1->L+2 (4%), HOMO->L+3 (4%)
8	40673.7333	245.86	0.0508	H-4->LUMO (10%), H-2->LUMO (19%), HOMO->L+2 (39%) H-3->LUMO (7%), H-2->L+1 (8%), H-1->L+2 (4%), H-1->L+3 (3%)
9	41244.77384	242.45	0.0549	H-2->L+1 (39%), H-1->L+2 (16%), HOMO->L+2 (15%), HOMO->L+3 (12%) H-4->LUMO (4%), H-3->LUMO (2%), H-1->L+3 (5%)
10	41696.44432	239.83	0.5151	**H-1->L+2 (62%)**, HOMO->L+2 (19%) H-4->L+1 (3%), H-2->L+1 (7%)
11	43654.75847	229.07	0.0125	H-2->L+1 (15%), H-1->L+3 (27%), HOMO->L+3 (37%) H-4->LUMO (2%), H-4->L+1 (2%), H-1->L+2 (3%), HOMO->L+6 (4%)
12	44448.40803	224.98	0.0338	H-1->L+3 (52%), HOMO->L+3 (35%) H-3->L+1 (2%), H-2->LUMO (3%), HOMO->L+6 (2%)
13	45300.93606	220.75	0.0295	H-5->LUMO (28%), H-4->LUMO (28%), H-3->LUMO (10%), H-3->L+1 (18%) H-5->L+1 (8%)
14	45539.67617	219.59	0.031	H-5->LUMO (21%), H-3->LUMO (11%), H-3->L+1 (49%) H-6->LUMO (2%), H-4->LUMO (6%), H-4->L+1 (2%)
15	46483.34485	215.13	0.0312	H-4->L+1 (28%), HOMO->L+4 (49%) H-5->LUMO (5%), H-5->L+1 (2%), H-4->LUMO (3%), H-1->L+4 (3%), HOMO->L+5 (3%)
16	46508.34804	215.02	0.041	H-4->L+1 (37%), HOMO->L+4 (37%) H-5->LUMO (6%), H-5->L+1 (3%), H-4->LUMO (4%), H-1->L+4 (2%)
17	47793.18924	209.23	0.004	H-1->L+4 (86%) H-3->LUMO (3%), HOMO->L+5 (4%)
18	48163.39773	207.63	0.0057	H-6->LUMO (55%), H-6->L+1 (30%) H-5->LUMO (3%), H-5->L+1 (9%)
19	48396.49196	206.63	0.1796	H-5->L+1 (49%), HOMO->L+6 (14%) H-7->LUMO (3%), H-6->LUMO (6%), H-6->L+1 (5%), H-5->LUMO (6%), H-4->L+1 (8%), H-2->L+2 (4%)
20	49198.20706	203.26	0.0062	HOMO->L+5 (86%) HOMO->L+4 (7%)
21	50046.70232	199.81	0.1694	H-2->L+2 (24%), HOMO->L+6 (42%) H-8->LUMO (9%), H-8->L+1 (3%), H-6->LUMO (3%), H-6->L+1 (8%), H-5->L+1 (2%)
22	50068.47929	199.73	0.0004	H-1->L+5 (21%), HOMO->L+7 (67%) H-1->L+4 (3%), HOMO->L+9 (3%)
23	50347.54712	198.62	0.0899	H-8->LUMO (23%), H-7->LUMO (10%), H-6->L+1 (19%) H-8->L+1 (7%), H-6->LUMO (4%), H-5->L+1 (3%), H-2->L+2 (8%), H-1->L+6 (9%), HOMO->L+6 (8%)
24	50589.51345	197.67	0.0009	H-1->L+5 (68%), HOMO->L+7 (21%) HOMO->L+8 (3%)
25	50775.02097	196.95	0.0267	H-7->LUMO (57%), H-1->L+6 (13%) H-8->LUMO (7%), H-6->L+1 (3%), H-5->L+1 (3%), H-2->L+2 (4%), HOMO->L+6 (3%)
26	51223.46523	195.22	0.0025	H-1->L+7 (83%) H-1->L+6 (7%)
27	51564.63775	193.93	0.0791	H-7->LUMO (15%), H-1->L+6 (56%) H-2->L+3 (9%), H-1->L+7 (8%)
28	52228.43205	191.47	0.0007	HOMO->L+8 (81%) HOMO->L+7 (3%), HOMO->L+9 (4%), HOMO->L+11 (5%)
29	52451.84763	190.65	0.0361	H-8->LUMO (41%), H-7->L+1 (16%), H-6->LUMO (12%), H-6->L+1 (17%) H-2->L+2 (2%)
30	52782.53494	189.46	0.0384	H-7->L+1 (70%) H-8->LUMO (7%), H-6->LUMO (2%), H-6->L+1 (4%), H-2->L+3 (3%)
31	53177.74661	188.05	0.0201	HOMO->L+8 (10%), HOMO->L+9 (57%), HOMO->L+11 (14%) H-2->L+2 (4%)
32	53689.10212	186.26	0.0009	H-1->L+8 (88%) H-1->L+5 (2%)
33	54097.21866	184.85	0.0932	H-2->L+2 (26%), H-2->L+3 (15%), HOMO->L+10 (18%) H-7->LUMO (2%), H-7->L+1 (2%), H-5->L+1 (3%), H-4->L+3 (2%), H-1->L+3 (2%), HOMO->L+6 (8%), HOMO->L+9 (5%)
34	54219.81494	184.43	0.0056	H-8->L+1 (71%) H-9->L+1 (2%), H-8->LUMO (3%), H-6->L+1 (2%), H-2->L+3 (5%)
35	54609.38072	183.12	0.0182	H-2->L+3 (13%), H-1->L+9 (28%) H-8->L+1 (8%), H-2->L+2 (6%), H-1->L+11 (8%), HOMO->L+6 (2%), HOMO->L+9 (8%), HOMO->L+10 (8%), HOMO->L+11 (4%)
36	54789.24236	182.52	0.0148	H-1->L+9 (39%), H-1->L+11 (10%), HOMO->L+10 (21%) H-2->L+2 (6%), H-2->L+3 (5%), HOMO->L+6 (2%), HOMO->L+11 (2%)
37	55043.30701	181.68	0.012	HOMO->L+9 (14%), HOMO->L+11 (67%) H-2->L+2 (2%), HOMO->L+10 (2%)
38	55525.62656	180.10	0.1341	H-2->L+3 (34%), HOMO->L+10 (43%) H-7->LUMO (3%), H-1->L+6 (3%), H-1->L+9 (4%)
39	55913.57924	178.85	0.0023	H-1->L+9 (20%), H-1->L+11 (67%) H-1->L+12 (2%)
40	56251.52554	177.77	0.0141	H-1->L+10 (90%) HOMO->L+14 (3%)
41	56750.78273	176.21	0.0006	HOMO->L+12 (54%), HOMO->L+13 (29%) H-2->L+4 (4%)
42	56862.08724	175.86	0.0198	H-9->LUMO (24%), H-3->L+2 (44%) H-4->L+2 (4%), H-4->L+3 (4%), H-3->L+3 (9%)
43	57047.59476	175.29	0.0013	H-9->LUMO (50%), H-3->L+2 (20%) H-11->LUMO (4%), H-11->L+1 (4%), H-9->L+1 (5%), H-8->L+1 (2%)
44	57431.51467	174.12	0.0044	H-4->L+2 (67%) H-11->LUMO (2%), H-3->L+2 (4%), H-2->L+6 (3%), HOMO->L+14 (8%)
45	57548.46506	173.77	0.0024	HOMO->L+12 (34%), HOMO->L+13 (57%) H-1->L+13 (2%)
46	57669.44823	173.40	0.0052	H-2->L+4 (64%) H-11->LUMO (3%), H-1->L+12 (9%), H-1->L+13 (3%), HOMO->L+12 (5%), HOMO->L+13 (3%)
47	57758.16922	173.14	0.0054	H-11->LUMO (31%), H-11->L+1 (16%), HOMO->L+14 (27%) H-10->LUMO (6%), H-9->LUMO (5%), H-2->L+4 (5%)
48	57808.17559	172.99	0.0221	H-11->LUMO (12%), H-4->L+2 (10%), HOMO->L+14 (55%) H-11->L+1 (7%), H-10->LUMO (3%), H-1->L+10 (2%)
49	58159.02677	171.94	0.0014	H-2->L+4 (15%), H-1->L+12 (40%), H-1->L+13 (28%) HOMO->L+15 (4%)
50	58534.88113	170.84	0.0269	H-10->LUMO (13%), H-5->L+2 (24%), H-3->L+2 (13%), H-3->L+3 (22%) H-5->L+3 (4%), H-4->L+3 (7%), H-2->L+6 (3%)

Table SI.5. Theoretical data of the 50 electronic transitions calculated for the cationic species of 8-nitroharmine (**9C**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	25255.63884	395.95	0.0958	**HOMO->LUMO (95%)** HOMO->L+1 (2%)
2	27977.76003	357.43	0.1098	**H-1->LUMO (94%)**
3	30527.27858	327.58	0.1715	**HOMO->L+1 (91%)** H-1->L+1 (3%), H-1->L+2 (3%)
4	32525.1139	307.45	0.0693	H-4->LUMO (16%), H-3->LUMO (26%), H-2->LUMO (23%), H-1->L+1 (21%) H-4->L+1 (2%), H-3->L+1 (2%), H-2->L+1 (2%),
5	33355.86497	299.80	0.2774	**H-1->L+1 (69%)** H-4->LUMO (5%), H-3->LUMO (9%), H-2->LUMO (8%), HOMO->L+1 (2%), HOMO->L+2 (3%)
6	36227.19873	276.04	0.0038	H-6->LUMO (11%), H-5->LUMO (24%), H-4->LUMO (44%) H-5->L+1 (3%), H-4->L+1 (3%), H-3->LUMO (3%), H-2->LUMO (6%)
7	37886.28119	263.95	0.0387	H-3->LUMO (21%), H-2->LUMO (60%) H-6->LUMO (5%), H-5->LUMO (5%), H-4->LUMO (2%), H-3->L+1 (2%)
8	40110.75831	249.31	0.1109	H-2->L+1 (17%), HOMO->L+2 (72%) H-1->L+2 (3%)
9	41659.34281	240.04	0.269	**H-2->L+1 (60%)**, HOMO->L+2 (16%) H-1->L+2 (5%), H-1->L+3 (3%), HOMO->L+3 (5%)
10	42123.91816	237.39	0.0236	H-6->LUMO (17%), H-5->LUMO (11%), H-4->LUMO (18%), H-3->LUMO (31%) H-8->LUMO (4%), H-7->LUMO (4%), H-1->L+2 (
11	42871.59412	233.25	0.3353	**H-1->L+2 (72%)** H-6->LUMO (2%), H-4->LUMO (3%), H-3->L+1 (6%), H-2->L+1 (5%), HOMO->L+1 (2%)
12	44098.36341	226.77	0.0074	HOMO->L+3 (79%) H-2->L+1 (8%), H-1->L+5 (4%)
13	45496.12223	219.80	0.1916	**H-3->L+1 (71%)** H-6->LUMO (2%), H-4->LUMO (3%), H-4->L+1 (4%), H-3->LUMO (3%), H-1->L+2 (4%), H-1->L+3 (6%)
14	46008.28429	217.35	0.0344	H-8->LUMO (14%), H-7->LUMO (57%), H-6->LUMO (21%) H-4->L+1 (3%)
15	46830.96981	213.53	0.0316	H-1->L+3 (70%) H-3->L+1 (6%), HOMO->L+3 (3%), HOMO->L+4 (4%), HOMO->L+5 (5%)
16	47128.5884	212.19	0.0091	HOMO->L+4 (86%) H-1->L+3 (3%), HOMO->L+6 (5%)
17	47268.92887	211.56	0.0385	H-4->L+1 (74%) H-7->LUMO (9%), H-4->LUMO (4%), H-1->L+3 (2%)
18	47628.65214	209.96	0.0436	H-6->LUMO (18%), H-5->LUMO (38%), H-5->L+1 (26%) H-7->LUMO (6%), H-4->L+1 (2%), H-1->L+3 (3%)
19	48269.05636	207.17	0.0074	H-8->LUMO (39%), HOMO->L+5 (35%) H-7->LUMO (7%), H-5->LUMO (2%), H-5->L+1 (5%), H-1->L+3 (3%)
20	48791.70363	204.95	0.0022	H-1->L+4 (81%) H-8->LUMO (3%), H-1->L+6 (2%), HOMO->L+6 (8%)
21	49541.79925	201.85	0.0947	H-8->LUMO (20%), H-1->L+5 (10%), HOMO->L+5 (35%) H-7->LUMO (5%), H-5->L+1 (4%), H-2->L+2 (4%), H-1->L+3 (3%)
22	49774.08692	200.91	0.0568	H-6->L+1 (41%), H-5->L+1 (20%), H-2->L+2 (10%) H-8->LUMO (6%), H-7->L+1 (2%), H-6->LUMO (8%), HOMO->L+6 (4%)
23	49855.54892	200.58	0.0365	HOMO->L+6 (69%) H-8->LUMO (3%), H-6->L+1 (5%), H-1->L+4 (5%), H-1->L+5 (7%), HOMO->L+4 (6%)
24	50253.98681	198.99	0.1478	H-2->L+2 (14%), H-1->L+5 (53%) H-8->LUMO (4%), H-7->LUMO (4%), H-6->L+1 (2%), HOMO->L+3 (3%), HOMO->L+5 (8%),
25	50678.23444	197.32	0.0065	HOMO->L+7 (92%)
26	51304.92723	194.91	0.061	H-7->L+1 (22%), H-6->L+1 (16%), H-5->L+1 (20%), H-2->L+2 (23%) H-6->LUMO (4%), H-5->LUMO (3%), H-1->L+6 (3%)
27	51626.74245	193.70	0.0024	H-1->L+6 (80%) H-7->L+1 (4%), H-1->L+4 (2%), H-1->L+5 (3%), HOMO->L+8 (4%)
28	51940.49212	192.53	0.0616	H-7->L+1 (57%), H-5->L+1 (16%) H-6->LUMO (3%), H-6->L+1 (7%), H-5->LUMO (6%)
29	52838.1872	189.26	0.0051	H-1->L+7 (93%)
30	53112.4157	188.28	0.0016	HOMO->L+8 (89%) H-1->L+6 (4%)
31	53971.39617	185.28	0.0267	H-8->L+1 (16%), H-2->L+2 (12%), HOMO->L+9 (20%), HOMO->L+10 (11%), HOMO->L+11 (11%) H-6->L+1 (7%), H-1->L+5 (
32	54190.77898	184.53	0.0098	H-8->L+1 (13%), HOMO->L+9 (64%) H-6->L+1 (3%), H-2->L+2 (5%)
33	54699.71482	182.82	0.0029	H-9->LUMO (18%), H-8->L+1 (27%), HOMO->L+10 (25%) H-9->L+1 (3%), H-1->L+8 (7%), HOMO->L+9 (4%), HOMO->L+11 (
34	54772.30472	182.57	0.0238	H-9->LUMO (54%), H-8->L+1 (23%) H-9->L+1 (7%), H-2->L+3 (3%)
35	54985.23509	181.87	0.0677	H-2->L+2 (12%), HOMO->L+10 (33%) H-9->LUMO (6%), H-8->L+1 (7%), H-7->L+1 (4%), H-6->L+1 (4%), H-3->L+2 (3%),
36	55119.12312	181.43	0.0274	H-1->L+8 (71%) H-9->LUMO (2%), H-8->L+1 (3%), H-2->L+3 (8%)
37	55261.0767	180.96	0.0515	H-3->L+2 (53%), H-2->L+3 (22%) H-3->L+3 (6%), H-1->L+8 (8%)
38	55580.47226	179.92	0.0071	HOMO->L+10 (17%), HOMO->L+11 (65%) H-3->L+2 (3%), H-2->L+3 (5%)
39	56007.13955	178.55	0.0254	H-11->LUMO (13%), H-10->LUMO (53%) H-8->L+1 (3%), H-3->L+2 (7%), H-2->L+3 (9%), HOMO->L+11 (4%)
40	56420.90197	177.24	0.0026	H-1->L+9 (81%) H-1->L+10 (3%), H-1->L+11 (4%)
41	56752.39584	176.20	0.013	H-11->LUMO (25%), H-1->L+10 (31%) H-9->L+1 (3%), H-3->L+2 (5%), H-2->L+3 (6%), H-1->L+9 (4%), H-1->L+11 (3%),
42	56891.1232	175.77	0.0069	H-11->LUMO (38%), H-10->LUMO (13%), H-1->L+10 (31%) H-9->L+1 (4%)
43	57246.81371	174.68	0.0559	H-10->LUMO (12%), H-2->L+3 (11%), H-1->L+11 (13%) H-4->L+2 (5%), H-3->L+2 (8%), H-1->L+9 (3%), H-1->L+10 (9%
44	57353.27889	174.36	0.0045	H-1->L+10 (13%), H-1->L+11 (55%), HOMO->L+14 (10%) HOMO->L+13 (4%)
45	57606.53698	173.59	0.0379	H-4->L+2 (14%), HOMO->L+12 (41%), HOMO->L+14 (13%) H-10->LUMO (4%), H-4->L+3 (2%), H-3->L+2 (3%), H-2->L+3 (
46	57729.13326	173.22	0.0047	H-4->L+2 (62%) H-11->LUMO (4%), H-10->LUMO (2%), H-4->L+3 (4%), H-3->L+2 (3%), H-2->L+3 (5%), HOMO->L+12 (4%
47	57959.00127	172.54	0.008	H-2->L+4 (13%), HOMO->L+13 (59%) H-2->L+3 (2%), H-1->L+9 (3%), H-1->L+11 (2%), HOMO->L+12 (8%)
48	58157.41366	171.95	0.0026	H-2->L+4 (36%), HOMO->L+12 (25%), HOMO->L+14 (13%) H-2->L+5 (5%), H-1->L+10 (3%), H-1->L+11 (4%), H-1->L+12
49	58296.94757	171.54	0.0037	H-2->L+4 (32%), HOMO->L+13 (11%), HOMO->L+14 (43%) HOMO->L+12 (4%)
50	58438.0946	171.12	0.003	H-9->LUMO (12%), H-9->L+1 (71%) H-14->LUMO (2%), H-11->LUMO (8%)

Table SI.6. Theoretical data of the 50 electronic transitions calculated for the cationic species of 6,8-dinitroharmine (**10C**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	26230.76314	381.23	0.131	**HOMO->LUMO (95%)** H-1->L+2 (2%)
2	27959.20928	357.66	0.068	**H-1->LUMO (91%)** HOMO->L+1 (3%)
3	28889.16654	346.15	0.1045	**HOMO->L+1 (76%)** H-5->L+1 (2%), H-4->L+1 (2%), H-2->L+1 (5%), H-1->LUMO (2%), H-1->L+1 (9%)
4	30966.04419	322.93	0.0164	H-1->L+1 (74%), HOMO->L+2 (11%) H-2->L+1 (3%), HOMO->L+1 (4%)
5	32219.42978	310.37	0.0524	**HOMO->L+2 (80%)** H-4->LUMO (3%), H-1->L+1 (7%), H-1->L+3 (2%)
6	32450.10434	308.17	0.0346	H-5->LUMO (10%), H-4->LUMO (40%), H-2->LUMO (17%) H-4->L+1 (4%), H-4->L+2 (4%), H-3->LUMO (3%), H-1->L+1 (6%), HOMO->L+2 (3%)
7	33948.68247	294.56	0.277	H-2->L+1 (10%), **H-1->L+2 (66%)** H-5->L+1 (4%), H-4->LUMO (3%), H-4->L+1 (5%), HOMO->L+3 (2%)
8	34912.51501	286.43	0.2185	H-4->L+1 (14%), H-2->L+1 (20%), H-1->L+2 (20%), HOMO->L+1 (10%), H-6->L+1 (3%), H-5->L+1 (9%), H-3->LUMO (5%), H-3->L+1 (3%), H-2->LUMO (4%)
9	35348.05441	282.90	0.0315	H-8->LUMO (13%), H-3->LUMO(32%), H-2->LUMO(10%), H-9->LUMO(8%), H-5->LUMO(9%), H-4->LUMO(4%), H-4->L+1(3%), H-2->L+1(4%), H-1->L+2(2%)
10	36257.04125	275.81	0.0071	H-6->L+1 (23%), H-3->L+1 (45%) H-8->L+1 (7%), H-7->L+1 (2%), H-5->L+1 (9%), H-2->L+1 (3%)
11	37018.42863	270.14	0.0217	H-4->LUMO (10%), H-2->LUMO (63%) H-9->LUMO (5%), H-8->LUMO (4%), H-3->LUMO (9%)
12	39653.44195	252.18	0.0138	H-9->LUMO (13%), H-8->LUMO (16%), H-3->LUMO (44%) H-10->LUMO (2%), H-7->LUMO (3%), H-5->LUMO (7%), H-4->LUMO (5%)
13	41072.97774	243.47	0.0168	H-5->LUMO (15%), H-4->LUMO (13%), H-4->L+1 (11%), H-2->L+1 (28%), H-2->L+2 (10%), H-6->LUMO(3%), H-5->L+1(5%), H-1->L+3(3%), HOMO->L+3(4%)
14	41610.94955	240.32	0.0492	H-5->LUMO (15%), H-2->L+2 (56%) H-9->LUMO (4%), H-6->LUMO (4%), H-4->LUMO (2%), H-1->L+3 (6%), HOMO->L+3 (5%)
15	41751.29002	239.51	0.0281	H-5->LUMO (20%), H-5->L+1(10%), H-4->L+1(15%), H-2->L+1 (22%), H-9->LUMO(3%), H-4->LUMO (7%), H-4->L+2 (2%), H-2->L+2(6%), HOMO->L+3(3%)
16	42578.81486	234.86	0.1006	H-6->LUMO (72%), HOMO->L+3 (11%) H-8->LUMO (5%), H-5->LUMO (8%)
17	42791.74523	233.69	0.2794	H-6->LUMO (12%), H-2->L+2 (10%), **HOMO->L+3 (58%)** H-3->L+2 (5%), H-1->L+2 (2%), H-1->L+4 (3%), HOMO->L+4 (2%)
18	43644.27326	229.13	0.1041	H-7->LUMO (13%), H-1->L+3 (58%) H-8->LUMO (3%), H-5->LUMO (2%), H-3->L+2 (6%), H-2->L+2 (4%)
19	43812.84314	228.24	0.0314	H-7->LUMO (26%), H-6->L+1 (13%), H-3->L+1 (19%), H-10->L+1 (4%), H-9->LUMO (7%), H-8->L+1 (3%), H-7->L+1 (2%), H-3->L+2 (4%), H-1->L+3 (9%)
20	44166.11398	226.42	0.0285	H-9->LUMO (12%), H-7->LUMO (24%), H-6->L+1 (14%), H-3->L+1 (23%), H-10->L+1(4%), H-8->L+1 (3%), H-7->L+1 (3%), H-3->L+2 (5%), H-1->L+3 (3%)
21	45051.71074	221.97	0.0805	H-4->L+2 (16%), H-3->L+2 (15%), HOMO->L+4 (39%) H-5->LUMO (3%), H-5->L+1 (4%), H-4->L+1 (6%), H-2->L+2 (4%), H-1->L+3 (4%)
22	45324.32614	220.63	0.0585	H-4->L+1 (10%), H-4->L+2 (26%), H-3->L+2 (31%), H-8->LUMO (2%), H-7->LUMO (3%), H-5->L+1 (9%), H-4->LUMO (2%), HOMO->L+4 (6%)
23	45494.50912	219.81	0.152	H-4->L+2(10%), H-3->L+2(18%), H-1->L+4(12%), HOMO->L+4(23%), H-9->L+2(2%), H-5->L+2(3%), H-1->L+3(4%), H-1->L+5(2%), HOMO->L+3(7%), HOMO->L+5(2%)
24	45791.32115	218.38	0.0189	H-5->L+1 (36%), H-4->L+1 (17%), H-4->L+2 (25%) H-6->L+1 (5%), H-3->L+2 (3%), HOMO->L+4 (3%)
25	46168.78862	216.60	0.0566	H-10->LUMO (61%), H-9->LUMO (14%) H-11->LUMO (4%), H-8->LUMO (4%), H-7->LUMO (5%), H-1->L+4 (2%)
26	46762.41268	213.85	0.0079	H-10->LUMO (14%), H-8->LUMO (17%), H-1->L+4 (34%) H-8->L+2 (4%), H-7->LUMO (5%), H-5->L+2 (4%), HOMO->L+4 (5%)
27	46905.97937	213.19	0.0352	H-9->LUMO (11%), H-8->LUMO (18%), H-1->L+4 (33%), H-10->LUMO (3%), H-8->L+2 (4%), H-7->LUMO (7%), H-7->L+2 (3%), HOMO->L+4 (6%)
28	48181.94848	207.55	0.0215	H-5->L+2 (72%) H-10->LUMO (2%), H-6->L+2 (3%), H-4->L+2 (6%), H-1->L+4 (2%), HOMO->L+5 (5%)
29	48739.27759	205.17	0.0017	H-8->L+1 (60%), H-7->L+1 (14%) H-9->L+1 (5%), H-7->L+2 (5%), H-6->L+1 (4%), H-6->L+2 (2%)
30	49249.82654	203.05	0.0114	H-9->L+1 (46%), H-8->L+2 (16%), H-7->L+1 (14%) H-9->LUMO (5%), H-9->L+2 (4%), H-6->L+2 (6%)
31	49384.52113	202.49	0.0015	H-11->LUMO (41%), HOMO->L+5 (30%) H-10->L+1 (5%), H-8->L+1 (3%), H-7->L+1 (3%)
32	49461.1438	202.18	0.0343	H-8->L+2 (15%), H-6->L+2 (67%) H-6->L+1 (3%), H-5->L+2 (6%)
33	49736.17886	201.06	0.0133	H-9->L+1 (25%), H-9->L+2 (15%), H-8->L+2 (13%), H-7->L+2 (16%), HOMO->L+6 (12%) H-6->L+2 (9%)
34	49783.76558	200.87	0.0052	HOMO->L+6 (74%) H-9->L+1 (4%), H-9->L+2 (3%), H-8->L+2 (3%), H-7->L+2 (4%), H-1->L+6 (4%)
35	50020.89258	199.92	0.0068	H-11->LUMO (16%), H-10->L+1 (34%), H-7->L+1 (21%) H-11->L+1 (2%), H-9->L+1 (8%), H-8->L+1 (8%), HOMO->L+5 (2%)
36	50495.14658	198.04	0.1964	H-9->L+2 (28%), H-7->L+2 (18%), H-1->L+5 (41%)
37	50664.52301	197.38	0.0361	H-11->LUMO (13%), H-2->L+3 (15%), H-1->L+5 (12%), H-1->L+6 (12%), HOMO->L+5 (19%), H-10->LUMO(2%), H-9->L+2(3%), H-7->L+2(8%), HOMO->L+4(2%)
38	50852.45019	196.65	0.0073	H-7->L+2(13%), H-2->L+3(12%), H-1->L+5(11%), H-1->L+6(33%), H-11->LUMO(2%), H-10->L+1(3%), H-9->L+2(4%), H-1->L+7(3%), HOMO->L+5(7%), HOMO->L+7(2%)
39	51236.3701	195.17	0.0419	H-11->LUMO (10%), H-1->L+6 (36%), HOMO->L+5 (21%) H-10->L+1 (3%), H-7->L+2 (4%), H-1->L+5 (2%), HOMO->L+6 (5%)
40	51867.09567	192.80	0.1026	H-8->L+2(18%), H-7->L+2(14%), H-2->L+3(25%), H-10->L+2(6%), H-9->LUMO(2%), H-9->L+2(9%), H-8->LUMO(2%), H-8->L+1(2%), H-7->LUMO(2%)
41	52199.39609	191.57	0.0678	H-10->L+1 (34%), H-7->L+1 (12%), H-6->L+1 (12%), H-11->L+1 (4%), H-9->L+1(2%), H-8->L+1 (3%), H-8->L+2(3%), H-7->L+2(3%), H-3->L+3(6%), H-3->L+4(4%)
42	52571.21768	190.22	0.0086	HOMO->L+7 (81%) H-1->L+7 (3%), HOMO->L+6 (2%), HOMO->L+8 (3%), HOMO->L+9 (2%)
43	52980.94733	188.75	0.0182	H-10->L+2 (73%) H-9->L+2 (4%), H-8->L+2 (7%), H-7->L+1 (3%)
44	53420.5195	187.19	0.0182	H-11->L+1 (75%) H-11->L+2 (2%), H-2->L+4 (8%)
45	53647.96784	186.40	0.0031	H-1->L+7 (65%), HOMO->L+8 (14%) H-1->L+6 (9%), H-1->L+10 (3%), HOMO->L+7 (2%)
46	53741.52816	186.08	0.0008	H-1->L+7 (12%), HOMO->L+8 (78%) H-1->L+10 (3%)
47	54594.05619	183.17	0.0076	H-9->L+2 (11%), H-2->L+3 (23%), H-1->L+5 (10%), H-13->LUMO (2%), H-12->LUMO (2%), H-11->L+2 (6%), H-10->L+2 (4%), H-8->L+2 (3%), H-2->L+4 (2%), H-1->L+8 (2%), HOMO->L+10 (5%)
48	55092.50683	181.51	0.1307	H-3->L+3 (19%), H-2->L+4 (34%), H-1->L+8 (12%), H-11->L+1 (3%), H-7->L+1 (3%), H-6->L+1 (3%), H-3->L+4 (6%), H-2->L+3 (3%), HOMO->L+10 (2%)
49	55154.61152	181.31	0.0195	H-1->L+8 (75%) H-3->L+3 (4%), H-2->L+4 (7%), HOMO->L+10 (4%)
50	55340.11904	180.70	0.0635	H-3->L+3 (42%), H-2->L+4 (23%) H-13->LUMO (2%), H-12->LUMO (7%), H-11->L+2 (3%), H-3->L+4 (2%), H-2->L+3 (3%)

Table SI.7. Theoretical data of the 50 electronic transitions calculated for the neutral species of 6-bromoharmine (**5N**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	31633.87126	316.12	0.0676	**HOMO->LUMO (93%)**, H-1->L+1 (5%)
2	34176.13082	292.60	0.2509	**H-1->LUMO (86%)**, HOMO->L+1 (11%)
3	37454.77457	266.99	0.0008	H-1->L+2 (15%), HOMO->L+2 (80%) H-2->L+2 (3%)
4	38975.93623	256.57	0.0026	H-3->LUMO (94%) H-3->L+1 (3%)
5	39321.94808	254.31	0.6989	**HOMO->L+1 (82%)**, H-1->LUMO (7%), H-1->L+4 (5%)
6	39944.6081	250.35	0.0001	H-1->L+2 (82%), HOMO->L+2 (14%)
7	40358.37052	247.78	0.2354	**H-1->L+1 (72%)**, HOMO->L+4 (11%), H-2->LUMO (7%), HOMO->LUMO (3%)
8	40659.21532	245.95	0.0002	HOMO->L+3 (94%)
9	41616.59543	240.29	0.0715	H-2->LUMO (68%), H-1->L+4 (12%) H-1->LUMO (2%),
10	42282.00283	236.51	0.0001	H-1->L+3 (88%) HOMO->L+5 (3%), HOMO->L+6 (3%)
11	43663.63057	229.02	0.3366	**HOMO->L+4 (66%)**, H-5->LUMO (3%), H-2->LUMO (9%), H-1->L+1 (9%), H-1->L+4 (3%), HOMO->L+8 (5%)
12	43712.02383	228.77	0.001	HOMO->L+6 (89%) H-1->L+3 (5%), HOMO->L+5 (3%)
13	43941.08529	227.58	0.0094	HOMO->L+5 (87%) H-1->L+3 (2%), HOMO->L+6 (4%)
14	45294.48362	220.78	0.0633	H-2->LUMO (10%), H-1->L+4 (74%) HOMO->L+4 (6%)
15	45422.72578	220.15	0.0014	H-1->L+5 (89%) H-1->L+6 (5%)
16	45615.49229	219.22	0.0006	H-3->L+1 (62%), H-3->L+4 (32%) H-1->L+6 (3%)
17	45675.98387	218.93	0.0039	H-1->L+6 (84%) H-3->L+1 (3%), H-1->L+5 (5%), H
18	46936.62844	213.05	0.0019	HOMO->L+7 (89%) H-1->L+6 (3%)
19	47595.58341	210.10	0.171	**HOMO->L+8 (75%)**, H-5->LUMO (4%), H-1->L+1 (2%), H-1->L+8 (4%), HOMO->L+10 (6%)
20	47739.95665	209.47	0.0002	H-4->LUMO (81%), H-2->L+2 (10%) H-4->L+1 (2%),
21	47898.04132	208.78	0.0002	H-4->LUMO (15%), H-2->L+2 (50%), HOMO->L+9 (24%)
22	48302.12509	207.03	0.0038	H-2->L+2 (29%), HOMO->L+9 (61%) H-1->L+7 (3%)
23	48390.03952	206.65	0.0018	H-2->L+1 (61%), H-1->L+8 (22%) H-5->LUMO (5%),
24	48580.38637	205.84	0.0001	H-1->L+7 (88%) H-1->L+11 (3%), HOMO->L+9 (4%)
25	48679.59256	205.42	0.076	H-5->LUMO (25%), H-1->L+8 (18%), HOMO->L+8 (11%), HOMO
26	49029.63718	203.96	0.0925	H-5->LUMO (40%), HOMO->L+10 (44%) H-2->L+4 (3%
27	49332.0951	202.71	0.0009	HOMO->L+11 (87%) HOMO->L+12 (4%), HOMO->L+14 (3
28	49838.61128	200.65	0.0034	H-1->L+9 (91%) HOMO->L+14 (2%)
29	50381.42241	198.49	0.0003	H-1->L+10 (77%) H-2->L+4 (4%), H-1->L+8 (9%)
30	50568.54304	197.75	0.0047	H-2->L+3 (63%), HOMO->L+12 (17%) HOMO->L+14 (4%
31	50625.8084	197.53	0.0461	H-6->LUMO (33%), H-2->L+1 (16%), H-2->L+4 (16%), H-1-
32	50675.00822	197.34	0.0013	H-3->L+1 (29%), H-3->L+4 (62%) H-3->LUMO (3%)
33	50964.56126	196.21	0.0069	H-1->L+11 (80%) H-2->L+3 (5%), H-1->L+7 (3%),
34	51287.18303	194.98	0.019	H-3->L+2 (11%), H-3->L+3 (60%), H-3->L+5 (14%)
35	51398.48754	194.56	0	H-2->L+3 (21%), H-1->L+11 (10%), HOMO->L+12 (37%), HOMO-
36	51450.10703	194.36	0.0232	H-4->L+2 (72%), H-3->L+3 (12%) H-3->L+2 (6%),
37	51724.33553	193.33	0.0114	HOMO->L+13 (82%) H-6->LUMO (5%), H-3->L+2 (3%)
38	51862.25634	192.82	0.0016	H-4->L+2 (12%), H-3->L+2 (74%) H-3->L+3 (3%),
39	52053.40974	192.11	0.1789	H-6->LUMO (48%), H-2->L+4 (24%) H-3->L+2 (5%),
40	52154.22904	191.74	0.0008	HOMO->L+12 (34%), HOMO->L+14 (60%)
41	52848.67241	189.22	0.0005	H-1->L+12 (69%), H-1->L+14 (19%) H-1->L+15 (3%
42	53043.05202	188.53	0.0698	H-2->L+4 (18%), H-1->L+13 (63%) H-5->LUMO (4%),
43	53109.99604	188.29	0.002	H-2->L+6 (11%), HOMO->L+15 (78%) H-2->L+5 (2%)
44	53407.61463	187.24	0.0213	H-5->L+1 (17%), H-2->L+4 (19%), H-1->L+13 (30%)
45	53566.50585	186.68	0.0002	H-2->L+6 (48%), H-1->L+14 (28%) H-1->L+12 (7%)
46	53697.97422	186.23	0.0009	H-2->L+5 (11%), H-2->L+6 (28%), H-1->L+12 (13%), H-1-
47	53806.05251	185.85	0	H-2->L+5 (78%) H-2->L+6 (4%), H-1->L+12 (2%), H-1-
48	54156.09714	184.65	0.0238	H-3->L+3 (13%), H-3->L+5 (19%), H-3->L+6 (51%), H-3->
49	54168.19545	184.61	0.0002	H-4->L+1 (91%) H-4->LUMO (3%), H-4->L+4 (3%),
50	54711.00658	182.78	0.024	HOMO->L+16 (88%) H-5->L+1 (3%)

Table SI.8. Theoretical data of the 50 electronic transitions calculated for the neutral species of 8-bromoharmine (**6N**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	31856.48028	313.91	0.0788	**HOMO->LUMO (85%)**, H-1->LUMO (9%), H-1->L+2 (4%)
2	34356.79901	291.06	0.28	**H-1->LUMO (76%)**, HOMO->L+2 (10%), HOMO->LUMO (9%)
3	36562.72538	273.50	0.0007	HOMO->L+1 (89%) H-2->L+1 (2%), H-1->L+1 (5%)
4	38875.11692	257.23	0.0026	H-3->LUMO (94%) H-3->L+2 (2%)
5	39136.44056	255.52	0.0002	H-1->L+1 (91%) HOMO->L+1 (5%)
6	39858.30677	250.89	0.5443	H-2->LUMO (23%), H-1->LUMO (11%), **HOMO->L+2 (62%)**
7	40749.54942	245.40	0.2533	**H-2->LUMO (40%)**, H-1->L+2 (16%), H-1->L+5 (13%), HOMO->L+2 (18%), HOMO->L+5 (6%)
8	40978.61087	244.03	0.0071	HOMO->L+3 (90%)
9	41228.64275	242.55	0.1068	H-2->LUMO (17%), H-1->L+2 (64%) H-1->L+5 (3%), HOMO->LUMO (3%),
10	42841.75161	233.42	0.0047	H-1->L+3 (88%) HOMO->L+4 (5%)
11	43890.27236	227.84	0.0001	HOMO->L+4 (79%), HOMO->L+6 (10%) H-1->L+3 (4%), HOMO->L+3 (3%)
12	44420.98518	225.12	0.0002	HOMO->L+6 (82%) HOMO->L+4 (9%)
13	44431.47038	225.07	0.06	HOMO->L+5 (74%) H-2->L+2 (4%), H-1->L+2 (6%), H-1->L+5 (6%), HOM
14	45349.32933	220.51	0.4532	H-2->LUMO (14%), **H-1->L+5 (62%)**, H-1->L+2 (3%), HOMO->L+2 (3%), HOMO->L+5 (7%), HOMO->L+9 (5%)
15	45479.99114	219.88	0.0003	H-3->L+2 (75%), H-3->L+5 (21%) H-1->L+4 (3%)
16	45564.67936	219.47	0.0025	H-1->L+4 (92%) H-3->L+2 (2%)
17	46393.81731	215.55	0.0004	H-1->L+6 (89%) H-1->L+8 (3%), HOMO->L+8 (3%)
18	46545.44954	214.84	0.0012	H-2->L+1 (88%) H-4->L+1 (2%), HOMO->L+1 (3%)
19	47283.44685	211.49	0	HOMO->L+7 (81%), HOMO->L+8 (10%) HOMO->L+3 (3%)
20	47361.68263	211.14	0.1283	**H-4->LUMO (69%)**, HOMO->L+9 (17%), H-1->L+5 (2%), H-1->L+9 (6%)
21	47800.44823	209.20	0.0977	H-4->LUMO (11%), H-2->L+2 (32%), HOMO->L+9 (50%)
22	48024.67037	208.23	0.0007	HOMO->L+7 (11%), HOMO->L+8 (80%) H-1->L+6 (3%)
23	48824.77236	204.81	0.0017	HOMO->L+10 (93%) HOMO->L+12 (2%)
24	48977.21115	204.18	0.0004	H-1->L+7 (83%) H-1->L+3 (3%), H-1->L+8 (7%), H-1->L+11 (2%)
25	49103.03364	203.65	0	H-5->LUMO (97%)
26	49676.49384	201.30	0.0001	H-1->L+7 (10%), H-1->L+8 (82%) H-1->L+6 (2%)
27	49749.08374	201.01	0.0235	H-2->L+2 (23%), H-1->L+9 (55%) H-1->L+5 (5%), HOMO->L+9 (5%),
28	49886.19799	200.46	0.0101	HOMO->L+11 (68%), HOMO->L+14 (21%) H-2->L+3 (4%)
29	50401.58627	198.41	0.0203	H-3->L+1 (87%) H-3->L+3 (3%), H-1->L+10 (3%)
30	50499.17935	198.02	0.0009	H-2->L+3 (69%), HOMO->L+11 (12%) H-2->L+7 (3%), HOMO->L+14 (6%
31	50530.63498	197.90	0.014	H-1->L+10 (74%), HOMO->L+12 (15%) H-3->L+1 (5%)
32	51209.75381	195.28	0.0058	H-1->L+10 (17%), HOMO->L+12 (76%) HOMO->L+10 (2%)
33	51619.48346	193.73	0.001	H-3->L+2 (17%), H-3->L+5 (67%) H-3->LUMO (3%), HOMO->L+14 (6%)
34	51694.49302	193.44	0	H-2->L+3 (12%), HOMO->L+14 (51%) H-3->L+5 (8%), H-1->L+11 (8%), H
35	51717.8831	193.36	0.0256	H-3->L+3 (67%), H-3->L+4 (16%) H-5->L+1 (2%), H-3->L+1 (5%), H
36	51888.87264	192.72	0.0012	H-1->L+11 (53%), HOMO->L+13 (31%) H-1->L+14 (6%), HOMO->L+14 (
37	52094.54401	191.96	0.0011	H-1->L+11 (21%), HOMO->L+13 (60%) HOMO->L+11 (3%), HOMO->L+14
38	52117.12754	191.88	0	H-5->L+1 (81%) H-3->L+3 (2%), H-2->L+5 (3%), H-1->L+9 (4%)
39	52603.47986	190.10	0.11	H-2->L+5 (54%), H-1->L+12 (19%) H-4->L+2 (9%), H-2->L+2 (6%), H-
40	52772.85629	189.49	0.0812	H-2->L+5 (25%), H-1->L+12 (52%) H-5->L+1 (5%), H-2->L+2 (2%),
41	52992.23909	188.71	0.0149	H-2->L+2 (23%), H-1->L+9 (15%), H-1->L+12 (27%) H-5->L+1 (6%),
42	53248.7234	187.80	0.0006	H-2->L+4 (16%), H-1->L+14 (69%) H-2->L+6 (3%), H-1->L+11 (4%)
43	53360.02791	187.41	0.0055	H-4->L+1 (18%), H-2->L+4 (42%), H-1->L+14 (13%) H-2->L+3 (3%),
44	53734.26917	186.10	0	H-4->L+1 (16%), H-2->L+4 (22%), H-1->L+13 (49%) H-1->L+14 (5%), H
45	53822.1836	185.80	0.0034	H-4->L+1 (34%), H-2->L+4 (12%), H-2->L+6 (16%), H-1->L+13 (31%)
46	53893.16039	185.55	0.0075	H-2->L+6 (35%), HOMO->L+15 (47%) H-4->L+1 (3%), H-1->L+13 (5%)
47	54034.30742	185.07	0.002	H-4->L+1 (20%), H-2->L+6 (31%), HOMO->L+15 (40%)
48	54378.70616	183.90	0.0296	H-6->LUMO (53%), H-4->L+2 (19%) H-3->L+6 (9%), H-2->L+5 (4%),
49	54646.48223	182.99	0.0175	H-3->L+3 (11%), H-3->L+6 (67%) H-6->LUMO (4%), H-3->L+4 (3%), H
50	54735.20322	182.70	0.0923	H-6->LUMO (29%), H-4->L+2 (47%), HOMO->L+17 (13%) H-4->L+5 (2%

15

Table SI.9. Theoretical data of the 50 electronic transitions calculated for the neutral species of 6,8-dibromoharmine (**7N**).

No.	Energy (cm^{-1})	λ (nm)	Osc.	Symmetry (% contribs)
1	30535.34413	327.48935	0.0793	**HOMO->LUMO (95%)**, H-1->L+2 (3%)
2	34397.12673	290.721957	0.0001	HOMO->L+1 (95%) H-2->L+1 (3%)
3	35298.85459	283.2953114	0.1235	**H-1->LUMO (72%)**, HOMO->L+2 (22%), H-2->LUMO (4%)
4	37648.34764	265.6159069	0.0022	H-3->LUMO (94%)
5	38179.86701	261.9181465	0.0005	H-1->L+1 (95%)
6	39392.92487	253.8526914	0.2262	**H-2->LUMO (63%)**, HOMO->L+2 (28%), H-1->L+4 (5%)
7	39726.8384	251.7189991	0.8291	**H-2->LUMO (25%)**, H-1->LUMO (23%), **HOMO->L+2 (47%)**
8	41298.81298	242.13771	0.0054	HOMO->L+3 (87%) HOMO->L+5 (4%)
9	42243.28822	236.7239962	0.0044	HOMO->L+5 (68%) H-1->L+2 (3%), HOMO->L+3 (6%), HOMO->L+4 (9%), HOMO->L+6 (3%), HOMO->L+7 (2%)
10	42347.33374	236.1423758	0.0451	H-1->L+2 (48%), HOMO->L+4 (30%), HOMO->L+5 (11%)
11	43557.16538	229.5833513	0.0002	H-2->L+1 (90%) HOMO->L+1 (3%)
12	44270.1595	225.8857911	0.2462	**HOMO->L+4 (20%)**, **HOMO->L+6 (35%)**, HOMO->L+8 (10%), H-4->LUMO (4%), H-2->L+2 (3%), H-1->L+2 (9%), H-1->L+4 (4%), HOMO->L+5 (4%)
13	44518.57826	224.6253225	0.003	H-5->LUMO (82%) H-6->LUMO (8%), H-4->LUMO (3%), HOMO->L+6 (3%)
14	44736.34796	223.5318808	0.0295	H-1->L+2 (10%), HOMO->L+4 (15%), HOMO->L+6 (37%), HOMO->L+7 (21%) H-4->LUMO (5%), H-1->L+3 (3%)
15	45078.32704	221.8360941	0.0256	HOMO->L+7 (59%) H-4->LUMO (4%), H-3->L+2 (6%), H-3->L+4 (3%), H-1->L+2 (5%), HOMO->L+4 (4%), HOMO->
16	45139.62517	221.534848	0.0013	H-3->L+2 (61%), H-3->L+4 (25%) HOMO->L+7 (7%)
17	45597.74809	219.309076	0.174	**H-4->LUMO (47%)**, **HOMO->L+8 (30%)**, H-1->L+3 (9%)
18	45771.96385	218.4743489	0.023	H-1->L+3 (58%), H-1->L+5 (18%) H-4->LUMO (3%), H-1->L+4 (4%), H-1->L+7 (2%), HOMO->L+8 (6%)
19	45948.59927	217.6344907	0.1443	**H-4->LUMO (26%)**, **HOMO->L+8 (36%)**, H-2->L+2 (8%), H-1->L+2 (8%), HOMO->L+4 (9%)
20	46555.93475	214.7953865	0.0009	H-6->LUMO (87%) H-5->LUMO (9%)
21	46694.66211	214.1572408	0.0026	H-1->L+3 (22%), H-1->L+5 (67%) H-1->L+4 (2%)
22	47462.50193	210.6926435	0.007	H-2->L+2 (48%), H-1->L+4 (13%), H-1->L+6 (10%) H-4->LUMO (2%), H-3->L+1 (3%), H-1->L+8 (6%), HOMO->L
23	47489.92478	210.57098	0.0237	H-3->L+1 (90%) H-2->L+2 (5%)
24	48073.06363	208.0166988	0.062	H-1->L+4 (57%) H-3->L+1 (3%), H-2->LUMO (2%), H-2->L+2 (7%), H-1->L+5 (4%), H-1->L+6 (5%), HOMO->L+8
25	48102.09959	207.8911333	0.0007	H-7->LUMO (95%)
26	48722.33995	205.244658	0.0006	H-5->L+1 (90%) HOMO->L+9 (3%)
27	48828.80513	204.7971474	0.0102	HOMO->L+9 (77%) H-5->L+1 (2%), H-4->L+1 (3%), H-1->L+4 (3%), H-1->L+6 (4%)
28	48919.94578	204.4155986	0.0007	H-4->L+1 (59%) H-8->L+1 (2%), H-2->L+3 (7%), H-2->L+5 (7%), HOMO->L+5 (3%), HOMO->L+9 (3%), HOMO->L
29	49182.88253	203.3227718	0.007	H-1->L+6 (13%), HOMO->L+10 (63%) H-4->L+1 (3%), H-1->L+7 (4%)
30	49461.1438	202.1789071	0.0123	H-8->LUMO (17%), H-1->L+6 (22%), HOMO->L+10 (12%), HOMO->L+11 (29%) H-2->L+2 (4%)
31	49669.23485	201.3318713	0.0016	H-1->L+6 (21%), HOMO->L+11 (45%) H-2->L+2 (3%), H-1->L+7 (7%), HOMO->L+10 (7%), HOMO->L+12 (2%)
32	49870.87345	200.5178435	0.0047	H-8->LUMO (13%), H-1->L+7 (55%), HOMO->L+11 (13%) H-6->L+1 (3%), HOMO->L+10 (3%)
33	50100.74147	199.5978444	0.0023	H-6->L+1 (40%), H-1->L+7 (18%), H-1->L+8 (17%) H-8->LUMO (7%), H-1->L+6 (6%)
34	50242.69505	199.0339091	0.0312	H-8->LUMO (17%), H-6->L+1 (39%), H-1->L+8 (23%) H-1->L+6 (5%), H-1->L+7 (2%)
35	50357.22577	198.5812333	0.0022	H-3->L+2 (26%), H-3->L+4 (54%) H-3->LUMO (2%), H-3->L+5 (5%), H-3->L+6 (5%), H-3->L+8 (2%)
36	50599.1921	197.631614	0.0089	H-2->L+3 (72%) H-4->L+1 (4%), H-2->L+5 (3%), HOMO->L+12 (5%), HOMO->L+14 (3%)
37	50814.54214	196.7940589	0.0062	HOMO->L+13 (79%) HOMO->L+14 (8%)
38	51000.85621	196.0751396	0.0032	H-7->L+1 (77%) H-8->LUMO (5%), H-7->L+5 (3%), H-2->L+4 (3%), H-1->L+8 (3%)
39	51232.33733	195.1892207	0.024	HOMO->L+12 (69%) H-7->L+1 (2%), H-2->L+3 (4%), H-2->L+4 (9%), HOMO->L+11 (4%)
40	51479.94954	194.2503847	0.1305	H-8->LUMO (15%), H-2->L+4 (31%), H-1->L+8 (15%), HOMO->L+12 (12%) H-7->L+1 (6%), H-5->L+2 (2%), H-2
41	51849.35147	192.8664432	0.0062	H-4->L+1 (15%), H-2->L+5 (63%) H-2->L+4 (7%), HOMO->L+13 (3%)
42	51930.00691	192.5668914	0.0365	H-3->L+3 (67%) H-3->L+5 (8%), H-3->L+6 (9%), H-3->L+8 (5%), H-2->L+4 (6%)
43	52263.92044	191.3365839	0.0424	H-5->L+2 (76%) H-5->L+4 (4%), H-2->L+4 (8%)
44	52330.05791	191.0947627	0.0449	H-4->L+2 (21%), H-2->L+4 (14%), H-1->L+8 (12%), H-1->L+9 (12%) H-9->LUMO (4%), H-8->LUMO (5%), H-5-
45	52762.37108	189.5290108	0.025	HOMO->L+14 (64%) H-4->L+2 (7%), H-2->L+3 (3%), H-2->L+5 (2%), H-2->L+8 (3%), H-1->L+9 (2%), HOMO->L+
46	52872.06248	189.1358031	0.1026	H-4->L+2 (34%), H-2->L+6 (17%), H-1->L+9 (10%), HOMO->L+14 (13%) H-5->L+2 (2%), H-2->L+4 (5%), H-2-
47	53401.96874	187.2590138	0.0922	H-4->L+2 (10%), H-2->L+6 (41%), H-1->L+9 (23%) H-6->L+2 (2%), H-4->L+4 (4%), H-2->L+4 (3%), H-2->L+
48	53434.23092	187.1459517	0.0027	H-6->L+2 (70%) H-6->L+4 (4%), H-5->L+2 (3%), H-3->L+6 (9%), H-3->L+8 (4%)
49	53687.48901	186.2631347	0.0184	H-2->L+7 (21%), HOMO->L+15 (28%) H-4->L+2 (4%), H-2->L+5 (3%), H-2->L+6 (5%), H-1->L+9 (6%), H-1->L+
50	53748.78715	186.0507098	0.0012	H-6->L+2 (15%), H-3->L+6 (38%), H-3->L+8 (15%) H-3->L+2 (3%), H-3->L+3 (2%), H-3->L+4 (6%), H-3->L+

Table SI.10. Theoretical data of the 50 electronic transitions calculated for the neutral species of 6-nitroharmine (**8N**).

No.	Energy (cm⁻¹)	λ (nm)	Osc.	Symmetry (% contribs)
1	24762.02752	403.84	0.0289	H-1->LUMO (17%), **HOMO->LUMO (81%)**
2	26277.5433	380.55	0.1916	**H-1->LUMO (80%)**, HOMO->LUMO (16%)
3	31800.02147	314.47	0.0145	H-5->LUMO (45%), H-3->LUMO (41%) HOMO->L+1 (7%)
4	33377.64194	299.60	0.1097	**HOMO->L+1 (80%)**, H-5->LUMO (5%), H-3->LUMO (2%), H-1->L+1 (5%), H-1->L+2 (3%)
5	34648.77172	288.61	0.0005	H-2->LUMO (96%) H-2->L+1 (2%)
6	35785.20691	279.45	0.0183	H-6->LUMO (30%), H-5->LUMO (26%), H-3->LUMO (24%) H-1->L+1 (9%), HOMO->L+1 (2%)
7	36023.14046	277.60	0.3951	**H-1->L+1 (74%)**, H-6->LUMO (7%), H-5->LUMO (3%), HOMO->L+1 (3%), HOMO->L+2 (6%)
8	37200.70993	268.81	0.1135	**H-6->LUMO (44%)**, H-5->LUMO (15%), **H-3->LUMO (29%)**, H-8->LUMO (4%), H-4->LUMO (3%)
9	38966.25757	256.63	0.0023	H-2->L+1 (92%) H-2->LUMO (2%), H-2->L+2 (3%)
10	40329.33456	247.96	0.0136	H-4->LUMO (85%) H-6->LUMO (4%), HOMO->L+2 (7%)
11	41734.35237	239.61	0.474	**HOMO->L+2 (73%)**, H-4->LUMO (7%), H-3->L+1 (2%), H-1->L+1 (6%), H-1->L+4 (2%), HOMO->L+4 (4%)
12	42388.46802	235.91	0.0533	H-3->L+1 (27%), H-1->L+2 (42%), H-1->L+4 (13%) HOMO->L+2 (3%), HOMO->L+4 (9%)
13	42622.3688	234.62	0.0007	HOMO->L+3 (95%)
14	43254.70747	231.19	0.1044	H-3->L+1 (43%), H-1->L+2 (34%), H-1->L+4 (10%) H-8->LUMO (2%), HOMO->L+4 (4%)
15	44696.82679	223.73	0.006	H-1->L+3 (91%) HOMO->L+5 (4%)
16	45525.15819	219.66	0.2013	H-1->L+2 (10%), **HOMO->L+4 (67%)**, H-8->LUMO (3%), H-4->L+1 (5%), H-1->L+4 (3%), HOMO->L+2 (3%), HOMO->L+8 (3%)
17	45851.81273	218.09	0.0037	HOMO->L+5 (23%), HOMO->L+6 (69%) H-1->L+3 (2%)
18	45987.31388	217.45	0.0006	H-2->L+2 (63%), H-2->L+4 (32%)
19	46195.40492	216.47	0.004	HOMO->L+5 (66%), HOMO->L+6 (26%)
20	46560.77408	214.77	0.1679	H-3->L+1 (18%), **H-1->L+4 (59%)**, H-8->LUMO (2%), H-1->L+2 (3%), HOMO->L+4 (6%)
21	47735.92388	209.49	0.0227	H-8->LUMO (61%), HOMO->L+8 (16%) H-7->LUMO (3%), H-6->LUMO (3%), H-3->L+1 (3%), H-1->L+5 (5%), HOMO->L+7 (2%)
22	47793.9958	209.23	0.0013	H-1->L+5 (85%) H-8->LUMO (3%), H-1->L+6 (4%), HOMO->L+7 (2%)
23	47937.56249	208.60	0.0007	H-1->L+6 (87%) H-1->L+3 (2%), H-1->L+5 (3%)
24	49013.5061	204.03	0.1382	H-8->LUMO (10%), H-4->L+1 (23%), HOMO->L+8 (49%) H-1->L+8 (5%), HOMO->L+10 (2%)
25	49109.48607	203.63	0.0306	HOMO->L+7 (80%) H-7->LUMO (3%), H-4->L+1 (2%), H-1->L+5 (2%)
26	49194.98084	203.27	0.0377	H-9->LUMO (18%), H-7->LUMO (48%) H-6->LUMO (5%), H-5->L+1 (9%), H-4->L+1 (3%), H-1->L+8 (3%)
27	49807.96221	200.77	0.09	H-4->L+1 (27%), HOMO->L+8 (12%), HOMO->L+9 (22%) H-9->LUMO (3%), H-7->LUMO (3%), H-3->L+2 (2%), H-1->L+4 (2%), H-1->L+8 (6%), HOMO->L+7 (4%), HOMO->L+10 (3%), HOMO->L+11 (4%)
28	50035.41056	199.86	0.0149	HOMO->L+9 (60%) H-9->LUMO (3%), H-5->L+1 (3%), H-4->L+1 (5%), H-3->L+2 (3%), H-1->L+8 (4%), HOMO->L+8 (3%)
29	50516.92355	197.95	0.0089	H-9->LUMO (11%), H-5->L+1 (70%) H-1->L+8 (3%), HOMO->L+10 (5%)
30	50566.12337	197.76	0.0046	H-1->L+7 (31%), H-1->L+8 (30%), H-1->L+11 (10%), H-4->L+1 (2%), H-3->L+2 (3%), H-1->L+9 (8%), HOMO->L+9 (3%), HOMO->L+10 (2%)
31	50778.24719	196.93	0.0211	HOMO->L+10 (77%) H-5->L+1 (2%), H-4->L+1 (4%), H-3->L+4 (2%), H-1->L+7 (3%), HOMO->L+12 (3%)
32	50950.04328	196.27	0.001	H-3->L+2 (17%), H-1->L+7 (31%), H-1->L+8 (15%), HOMO->L+11 (19%) H-4->L+1 (5%), H-2->L+3 (3%)
33	51158.13432	195.47	0.0037	H-1->L+7 (21%), HOMO->L+11 (61%) H-1->L+8 (2%), HOMO->L+9 (4%)
34	51447.68736	194.37	0.0001	H-2->L+2 (27%), H-2->L+4 (59%) H-9->LUMO (2%), H-2->L+1 (3%)
35	51607.38514	193.77	0.0114	H-9->LUMO (35%), H-7->LUMO (13%), H-1->L+9 (24%) H-5->L+1 (3%), H-3->L+2 (2%), H-2->L+4 (5%), H-1->L+11 (3%)
36	51621.90312	193.72	0.0181	H-9->LUMO (19%), H-7->LUMO (10%), H-1->L+9 (33%) H-5->L+1 (3%), H-3->L+2 (9%), H-2->L+3 (3%), H-1->L+7 (5%), H-1->L+8 (2%), H-1->L+11 (6%)
37	51977.59362	192.39	0.0249	H-2->L+3 (68%), H-2->L+5 (14%) H-4->L+1 (3%), H-3->L+2 (5%)
38	52414.74612	190.79	0.0225	H-6->L+1 (75%), H-3->L+2 (10%) H-1->L+9 (3%), H-1->L+11 (2%)
39	52551.86038	190.29	0.0017	H-1->L+10 (85%) H-1->L+8 (5%), HOMO->L+12 (2%)
40	52675.2632	189.84	0.0069	H-1->L+9 (17%), H-1->L+11 (55%) H-6->L+1 (7%), H-3->L+3 (3%), HOMO->L+13 (5%)
41	52918.03609	188.97	0.0001	H-3->L+3 (21%), HOMO->L+13 (21%), HOMO->L+14 (36%) H-1->L+11 (8%), HOMO->L+11 (2%), HOMO->L+15 (3%)
42	53566.50585	186.68	0.0101	H-3->L+3 (50%), HOMO->L+14 (33%) HOMO->L+12 (9%)
43	53621.35155	186.49	0.0165	HOMO->L+12 (73%) H-3->L+2 (2%), H-3->L+3 (5%), HOMO->L+10 (2%), HOMO->L+13 (4%), HOMO->L+14 (4%)
44	54151.25781	184.67	0.0005	H-3->L+3 (14%), HOMO->L+13 (64%), HOMO->L+14 (13%) HOMO->L+12 (3%)
45	54339.18499	184.03	0.1442	H-3->L+2 (15%), H-3->L+4 (41%) H-7->L+1 (5%), H-6->L+1 (4%), H-1->L+8 (8%), H-1->L+11 (4%), HOMO->L+12 (5%)
46	54658.58054	182.95	0.0018	H-2->L+5 (19%), H-2->L+6 (49%), H-2->L+7 (11%) H-3->L+4 (5%), H-2->L+3 (9%)
47	54834.40941	182.37	0.0286	H-7->L+1 (75%) H-12->LUMO (8%), H-10->LUMO (3%)
48	54969.91055	181.92	0.0453	H-3->L+4 (26%), HOMO->L+15 (24%) H-4->L+1 (3%), H-4->L+2 (6%), H-3->L+2 (7%), H-2->L+3 (2%), H-2->L+5 (4%)
49	55039.27424	181.69	0.0131	H-3->L+4 (11%), HOMO->L+15 (55%) H-4->L+2 (3%), H-3->L+2 (4%), H-1->L+13 (8%), HOMO->L+14 (3%)
50	55161.06395	181.29	0.0009	H-1->L+13 (32%), H-1->L+14 (48%) H-1->L+15 (4%), HOMO->L+15 (6%)

Table SI.11. Theoretical data of the 50 electronic transitions calculated for the neutral species of 8-nitroharmine (**9N**).

No.	Energy (cm^{-1})	λ (nm)	Osc.	Symmetry (% contribs)
1	23675.59871	422.38	0.1182	**HOMO->LUMO (92%)**, H-1->LUMO (7%)
2	25675.04714	389.48	0.0826	**H-1->LUMO (91%)**, HOMO->LUMO (7%)
3	31292.69874	319.56	0.0082	H-5->LUMO (50%), H-4->LUMO (33%), H-3->LUMO (10%)
4	32821.92593	304.67	0.0004	H-2->LUMO (98%)
5	34527.78855	289.62	0.0058	H-3->LUMO (26%), HOMO->L+1 (63%) H-5->LUMO (2%), H-1->L+2 (2%)
6	34685.87322	288.30	0.1395	**H-3->LUMO (54%)**, HOMO->L+1 (28%), H-6->LUMO (3%), H-5->LUMO (9%), H-1->L+2 (2%)
7	36100.56969	277.00	0.0079	H-6->LUMO (71%) H-7->LUMO (6%), H-5->LUMO (5%), H-4->LUMO (7%), H-3->LUMO (6%)
8	36619.99074	273.07	0.37	**H-1->L+1 (86%)**, HOMO->L+2 (9%)
9	39359.85614	254.07	0.0453	H-6->LUMO (10%), H-5->LUMO (27%), H-4->LUMO (50%) H-2->L+1 (8%)
10	39378.40689	253.95	0.0061	H-2->L+1 (87%) H-5->LUMO (3%), H-4->LUMO (4%)
11	42406.21221	235.81	0.6834	**HOMO->L+2 (84%)**, H-1->L+1 (7%), H-1->L+4 (2%)
12	43175.66514	231.61	0.0618	H-1->L+2 (77%), HOMO->L+4 (13%) H-8->LUMO (2%), HOMO->L+1 (3%)
13	43351.494	230.67	0.0101	HOMO->L+3 (94%) HOMO->L+5 (2%)
14	44182.24507	226.34	0.1297	**H-3->L+1 (61%)**, H-1->L+4 (23%), HOMO->L+4 (8%)
15	44918.62926	222.62	0.0011	H-1->L+3 (86%) HOMO->L+5 (9%)
16	45855.03895	218.08	0.0861	H-8->LUMO (24%), H-2->L+2 (18%), HOMO->L+4 (37%) H-3->L+1 (5%), H-2->L+4 (6%),
17	45919.56331	217.77	0.032	H-2->L+2 (54%), H-2->L+4 (20%), HOMO->L+4 (12%) H-8->LUMO (8%)
18	46338.97161	215.80	0.0007	HOMO->L+5 (75%), HOMO->L+6 (11%) H-1->L+3 (8%)
19	46720.47185	214.04	0.0008	HOMO->L+6 (85%) HOMO->L+5 (9%)
20	47301.9976	211.41	0.0186	H-9->LUMO (10%), H-7->LUMO (15%), H-3->L+1 (17%), H-1->L+4 (18%), HOMO->L+8 (10%)
21	47473.79369	210.64	0.1169	H-9->LUMO (15%), H-8->LUMO (35%), H-7->LUMO (13%) H-6->LUMO (4%), H-4->L+1 (3%)
22	47714.14691	209.58	0.0049	H-1->L+5 (91%) HOMO->L+7 (3%)
23	47919.01174	208.69	0.1181	H-9->LUMO (14%), **H-1->L+4 (44%)**, H-8->LUMO (5%), H-7->LUMO (7%), H-6->LUMO (2%), H-3->L+1(7%), H-1->L+2 (3%), HOMO->L+4 (7%)
24	48515.86201	206.12	0.0008	H-1->L+6 (87%) HOMO->L+9 (4%)
25	49263.53797	202.99	0.0547	H-9->LUMO (24%), H-7->LUMO (34%), HOMO->L+7 (14%) H-5->L+1 (7%), H-4->L+1 (4%)
26	49340.96719	202.67	0.0138	H-7->LUMO (10%), HOMO->L+7 (63%) H-9->LUMO (7%), H-1->L+5 (2%), HOMO->L+9 (5%)
27	49766.02138	200.94	0.0097	HOMO->L+8 (42%), HOMO->L+9 (10%) H-9->LUMO (3%), H-8->LUMO (7%), H-7->LUMO (3%)
28	50007.98771	199.97	0.0677	H-9->LUMO (10%), H-5->L+1 (11%), H-4->L+1 (55%) H-1->L+7 (4%), H-1->L+8 (6%), H
29	50088.64315	199.65	0.0042	HOMO->L+8 (24%), HOMO->L+9 (54%) H-1->L+6 (6%), H-1->L+8 (3%), HOMO->L+7 (5%)
30	50617.74286	197.56	0.013	H-1->L+7 (63%) H-5->L+1 (6%), H-1->L+6 (2%), H-1->L+8 (3%), H-1->L+9 (2%), H-1->
31	50924.23354	196.37	0.0817	H-5->L+1 (25%), H-1->L+8 (20%), H-1->L+9 (20%) H-9->LUMO (2%), H-3->L+2 (2%), H
32	51142.80979	195.53	0.0603	H-5->L+1 (27%), H-4->L+1 (10%), H-3->L+2 (24%), H-2->L+3 (10%) H-2->L+5 (3%), H
33	51579.15573	193.88	0.0002	H-1->L+8 (39%), H-1->L+9 (42%) H-1->L+7 (7%), HOMO->L+10 (5%)
34	51638.03421	193.66	0.0031	H-1->L+9 (10%), HOMO->L+10 (69%), HOMO->L+12 (10%) H-3->L+2 (4%)
35	52067.92772	192.06	0.0304	H-2->L+3 (66%), H-2->L+5 (10%) H-5->L+1 (4%), H-4->L+1 (3%), H-3->L+2 (5%), H-2
36	52400.22814	190.84	0.0027	HOMO->L+11 (77%), HOMO->L+14 (15%)
37	52613.15851	190.07	0.0004	H-2->L+2 (25%), H-2->L+4 (70%)
38	52809.95779	189.36	0.0119	H-1->L+10 (66%), HOMO->L+12 (15%) H-3->L+2 (7%), H-1->L+8 (2%)
39	53364.06069	187.39	0.0028	H-10->LUMO (61%), H-6->L+1 (10%) H-12->LUMO (2%), H-9->LUMO (3%), H-3->L+3 (4%)
40	53393.09665	187.29	0.0006	H-10->LUMO (13%), H-3->L+3 (20%), HOMO->L+14 (42%) H-1->L+11 (2%), HOMO->L+11 (
41	53595.54181	186.58	0.0089	H-10->LUMO (16%), H-6->L+1 (65%) H-7->L+1 (4%), HOMO->L+12 (3%)
42	53877.83586	185.61	0.0107	H-1->L+10 (13%), HOMO->L+12 (65%) H-6->L+1 (4%), HOMO->L+10 (7%)
43	54010.11078	185.15	0.0029	H-1->L+11 (42%), HOMO->L+13 (45%) H-3->L+3 (3%)
44	54194.00519	184.52	0.0009	H-3->L+3 (43%), H-1->L+11 (27%), HOMO->L+13 (14%) H-1->L+9 (2%), HOMO->L+14 (3%
45	54523.0794	183.41	0.0172	H-11->LUMO (20%), H-3->L+3 (13%), HOMO->L+13 (15%), HOMO->L+14 (12%) H-6->L+1 (
46	54559.37435	183.29	0.0164	H-11->LUMO (18%), H-3->L+3 (10%), H-1->L+11 (13%), HOMO->L+13 (19%), HOMO->L+14 (12%)
47	54969.91055	181.92	0.0064	H-11->LUMO (31%), H-1->L+12 (44%) H-3->L+2 (3%), H-2->L+6 (3%), H-1->L+10 (2%)
48	55085.24784	181.54	0.0016	H-2->L+6 (73%) H-2->L+3 (5%), H-2->L+8 (5%), H-2->L+9 (4%), H-1->L+12 (9%)
49	55185.26059	181.21	0.0018	H-1->L+13 (13%), H-1->L+14 (66%) H-1->L+11 (3%), H-1->L+12 (6%)
50	55351.4108	180.66	0.0048	H-11->LUMO (11%), H-3->L+2 (12%), H-1->L+12 (26%) H-7->L+1 (6%), H-5->L+2 (4%),

Table SI.12. Theoretical data of the 50 electronic transitions calculated for the neutral species of 6,8-dinitroharmine (**10N**).

No.	Energy (cm^{-1})	λ (nm)	Osc.	Symmetry (% contribs)
1	23241.67243	430.26	0.102	**HOMO->LUMO (99%)**
2	25877.4923	386.44	0.0613	H-1->LUMO (16%), **HOMO->L+1 (81%)**
3	27430.91613	364.55	0.1484	**H-1->LUMO (79%)**, HOMO->L+1 (14%)
4	29041.60533	344.33	0.0167	H-1->L+1 (89%) H-6->L+1 (4%)
5	30557.1211	327.26	0.0048	H-5->LUMO (15%), H-2->LUMO (63%) H-7->LUMO (5%), H-4->LUMO (8%), H-3->LUMO (4%)
6	30922.49025	323.39	0.0095	H-7->LUMO (10%), H-5->LUMO (32%), H-2->LUMO (33%) H-4->LUMO (9%), H-3->LUMO (9%)
7	31952.46026	312.96	0.0018	H-6->L+1 (36%), H-3->L+1 (44%) H-7->L+1 (2%), H-4->LUMO (3%), H-1->L+1 (4%), HOM
8	32679.97235	306.00	0.0045	H-5->LUMO (13%), H-4->LUMO (64%) H-10->LUMO (4%), H-4->L+1 (3%), H-3->LUMO (6%)
9	33947.06936	294.58	0.0013	H-2->L+1 (96%)
10	34080.15084	293.43	0.0506	H-5->LUMO (16%), H-3->LUMO (70%) HOMO->L+2 (5%)
11	34779.43353	287.53	0.0937	**HOMO->L+2 (87%)**, H-3->LUMO (4%), H-1->L+3 (3%)
12	35271.43173	283.52	0.0017	H-8->L+1 (17%), H-4->L+1 (59%) H-10->L+1 (7%), H-6->L+1 (4%), H-5->L+1 (3%), H-
13	37200.70993	268.81	0.0673	H-11->LUMO (15%), H-8->L+1 (11%), H-6->L+1 (19%), H-4->L+1 (12%), H-3->L+1 (17%)
14	37543.49556	266.36	0.0256	H-11->LUMO (25%), H-10->LUMO (10%), H-8->LUMO (14%), H-6->L+1 (15%), H-3->L+1 (16%)
15	38225.84061	261.60	0.0167	H-10->L+1 (18%), H-8->L+1 (27%), H-4->L+1 (14%), H-3->L+1 (13%) H-11->LUMO (2%),
16	38375.05318	260.59	0.0022	H-2->L+2 (94%) H-2->L+6 (2%)
17	38993.68042	256.45	0.3848	**H-1->L+2 (79%)**, HOMO->L+3 (10%), H-7->LUMO (4%)
18	39963.15885	250.23	0.027	H-6->LUMO (91%) H-7->LUMO (3%)
19	40813.26722	245.02	0.0747	H-7->LUMO (61%), H-5->LUMO (15%) H-8->LUMO (3%), H-6->LUMO (5%), H-5->L+1 (5%),
20	41704.50986	239.78	0.0015	H-5->L+1 (88%) H-8->L+1 (4%), H-7->LUMO (4%)
21	43257.93369	231.17	0.0214	H-10->LUMO (28%), H-8->LUMO (63%) H-11->LUMO (4%)
22	43676.53544	228.96	0.4128	H-7->L+1 (11%), **HOMO->L+3 (67%)**, H-1->L+2 (7%), HOMO->L+4 (5%)
23	44142.7239	226.54	0.0043	H-11->LUMO (10%), H-10->LUMO (15%), H-9->LUMO (72%)
24	44227.41211	226.10	0.1834	H-7->L+1 (69%), HOMO->L+3 (11%) H-8->L+1 (3%), H-3->L+2 (8%), H-1->L+2 (3%)
25	44604.87959	224.19	0.0314	H-7->L+1 (10%), H-3->L+2 (75%) H-1->L+4 (7%)
26	45492.89601	219.81	0.0143	HOMO->L+4 (28%), HOMO->L+5 (65%)
27	45878.42903	217.97	0.0014	H-2->L+3 (61%), H-2->L+4 (28%) H-2->L+5 (5%), HOMO->L+5 (3%)
28	46064.7431	217.09	0.1216	H-1->L+3 (32%), HOMO->L+4 (28%), HOMO->L+5 (17%) H-4->L+2 (9%)
29	46530.93156	214.91	0.0521	H-4->L+2 (80%) H-11->LUMO (4%), H-1->L+3 (4%), HOMO->L+4 (3%)
30	46921.30391	213.12	0.0017	H-10->L+1 (56%), H-9->L+1 (13%), H-8->L+1 (23%) H-11->L+1 (5%)
31	47528.63939	210.40	0.063	H-12->LUMO (17%), H-10->LUMO (11%), H-1->L+3 (12%), HOMO->L+4 (13%), HOMO->L+6 (12%)
32	47726.24523	209.53	0.1473	H-11->L+1 (12%), H-1->L+3 (13%), **HOMO->L+6 (31%)**, H-12->LUMO (8%), H-9->L+1 (3%), H-3->L+2 (3%), H-1->L+4 (8%), HOMO->L+4 (2%), HOMO->L+7 (3%), HOMO->L+8 (5%)
33	47737.53699	209.48	0.0125	H-11->L+1 (59%), H-9->L+1 (15%), HOMO->L+6 (15%) H-1->L+4 (2%)
34	48394.07229	206.64	0.0798	H-11->LUMO (20%), H-10->LUMO (17%), H-9->LUMO (14%) H-12->L+1 (2%), H-11->L+1 (
35	48911.07368	204.45	0.0016	HOMO->L+7 (54%), HOMO->L+8 (42%)
36	49212.72504	203.20	0.0394	H-12->LUMO (37%), H-5->L+2 (16%) H-12->L+1 (8%), H-1->L+3 (5%), HOMO->L+6 (2%),
37	49355.48517	202.61	0.0116	H-5->L+2 (11%), HOMO->L+6 (13%), HOMO->L+7 (20%), HOMO->L+8 (27%) H-12->LUMO (3
38	49689.39871	201.25	0.0964	H-12->LUMO (13%), H-12->L+1 (10%), H-5->L+2 (54%) H-7->L+2 (4%), H-1->L+3 (4%)
39	50007.98771	199.97	0.0064	H-1->L+4 (24%), H-1->L+5 (59%) H-1->L+9 (2%), HOMO->L+7 (7%)
40	50715.33594	197.18	0.0406	H-12->L+1 (10%), H-9->L+1 (36%) H-12->LUMO (6%), H-11->L+1 (8%), H-10->L+1 (4%)
41	50877.45338	196.55	0.0631	H-12->L+1 (15%), H-1->L+4 (33%), H-1->L+5 (19%) H-9->L+1 (4%), H-3->L+2 (3%), H
42	51421.07107	194.47	0.0456	H-12->L+1 (44%), H-9->L+1 (15%) H-12->LUMO (7%), H-11->L+1 (4%), H-10->L+1 (4%)
43	51928.3938	192.57	0.0147	H-7->L+2 (16%), H-3->L+3 (16%), H-1->L+6 (36%) H-6->L+2 (8%), H-1->L+7 (4%), H-
44	52035.66554	192.18	0.0003	HOMO->L+9 (60%), HOMO->L+10 (22%) HOMO->L+6 (2%), HOMO->L+8 (3%)
45	52240.53037	191.42	0.0006	H-2->L+3 (30%), H-2->L+4 (50%) H-13->LUMO (4%), H-2->L+5 (5%), H-2->L+6 (4%)
46	52402.64781	190.83	0.0354	H-6->L+2 (57%) H-13->LUMO (8%), H-7->L+2 (5%), H-2->L+5 (7%), H-1->L+4 (3%), H-
47	52501.854	190.47	0.0103	H-13->LUMO (41%), H-7->L+2 (10%), H-3->L+3 (10%) H-14->LUMO (9%), H-2->L+4 (4%)
48	52586.54222	190.16	0.0026	H-13->LUMO (27%), HOMO->L+9 (15%), HOMO->L+10 (42%)
49	52716.39748	189.69	0.0048	H-13->LUMO (12%), H-6->L+2 (18%), H-2->L+5 (21%), HOMO->L+10 (12%) H-14->LUMO (
50	53053.53723	188.49	0.0052	H-14->LUMO (25%), H-3->L+3 (15%), H-2->L+5 (38%) H-2->L+4 (4%), H-2->L+8 (4%)

**18. Molecular orbital diagram of neutral (N) and cationic (C) species of bromoharmines (5 - 7)**
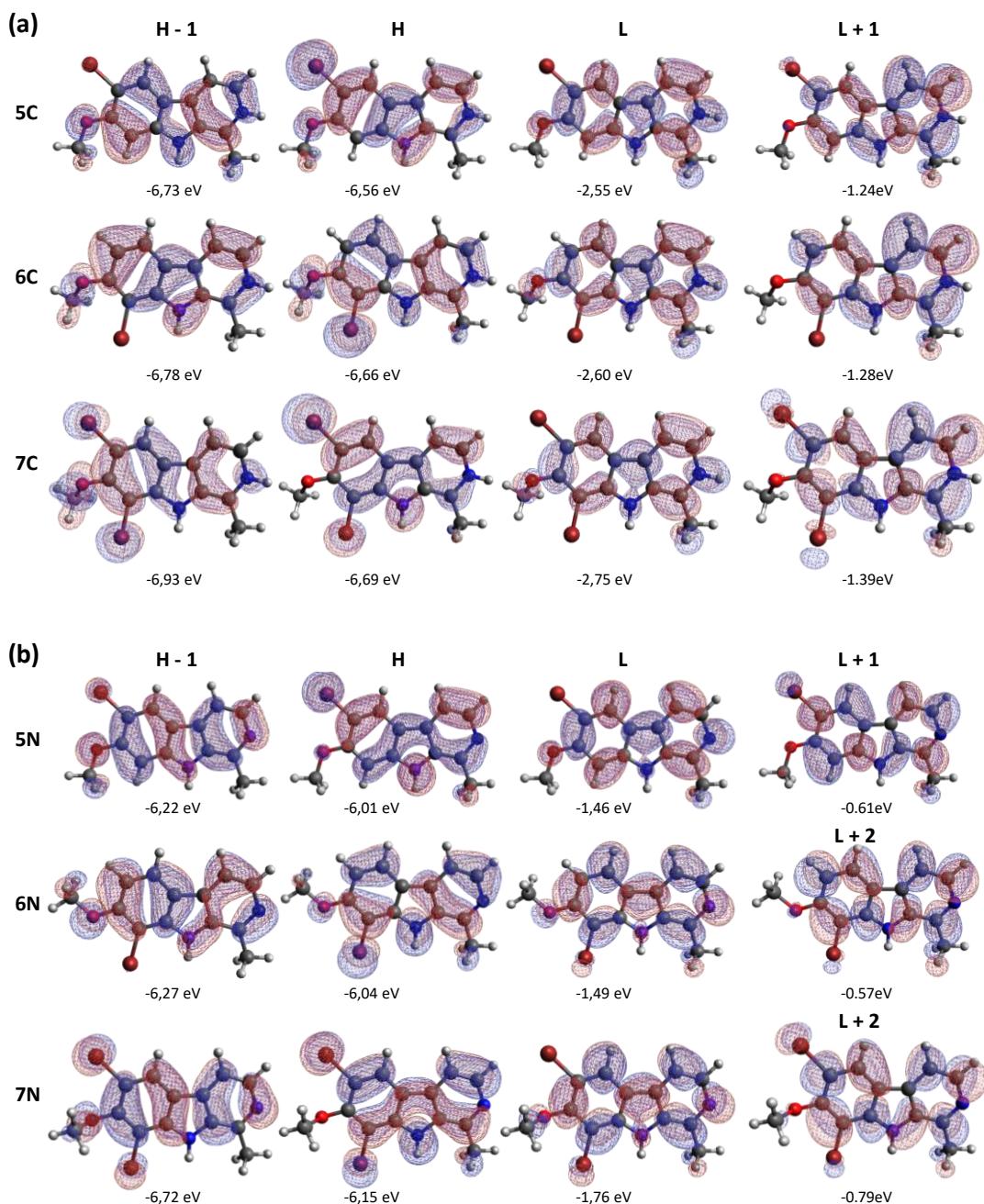
Figure SI.6. Molecular orbital diagram of **(a)** cationic (**C**) and **(b)** neutral (**N**) species of bromoharmines **5** – **7** (isovalue = 0.02 e$^{1/2}$ bohr$^{-3/2}$). HOMO-LUMO and HOMO–1-LUMO are the main transitions involved in the low energy absorption bands (300 nm < λ < 400 nm) of the compounds in H$_2$O. The vertical transition energies were calculated for the optimized ground-state geometry using TD-DFT calculations. All calculations are performed in water at the B3LYP/aug-cc-pVDZ level of theory using the polarizable continuum model.

19. Molecular orbital diagram of neutral (N) and cationic (C) species of nitroharmines (8 - 10)

(a)

(b)
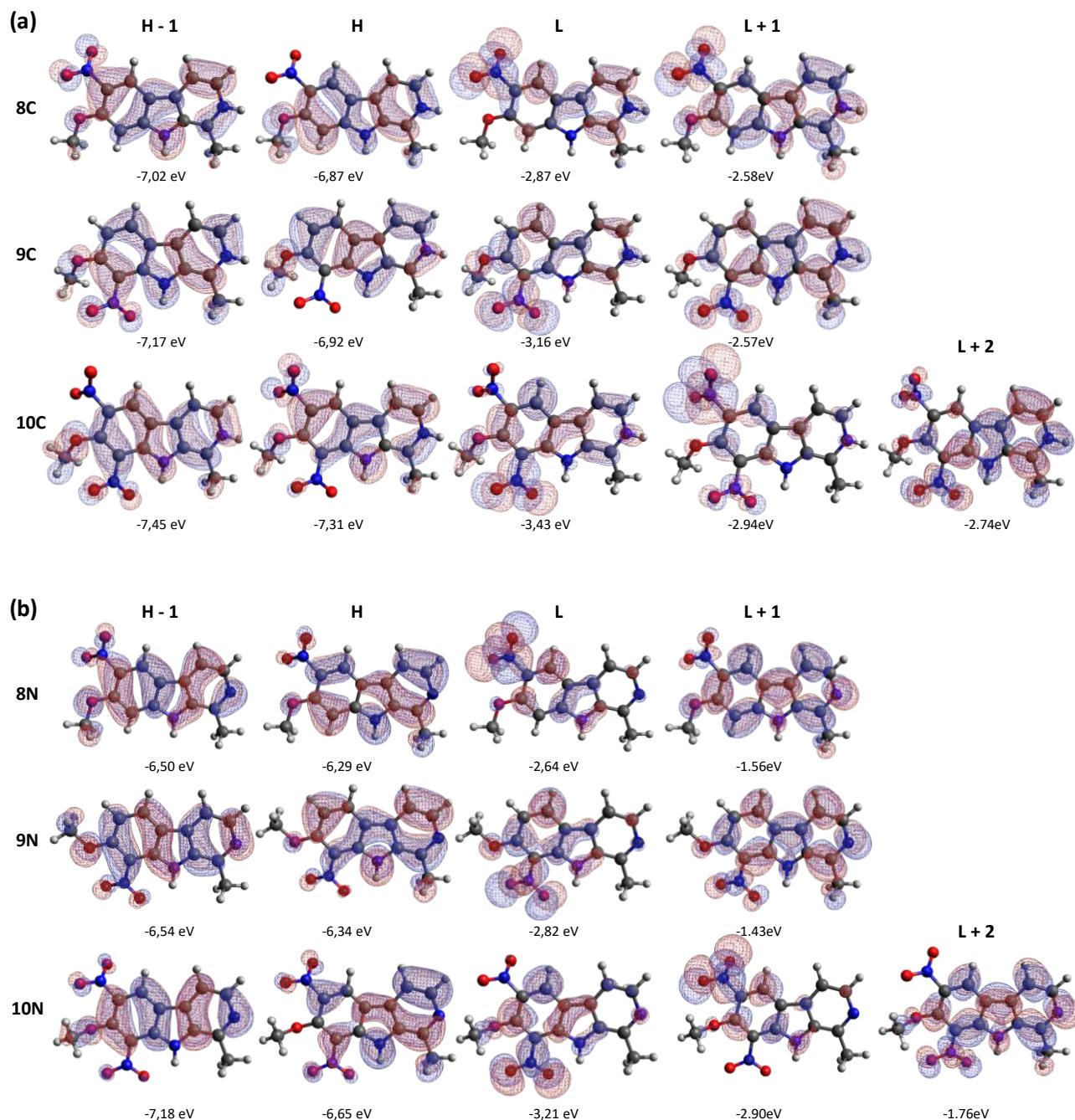
Figure SI.7. Molecular orbital diagram of **(a)** cationic (**C**) and **(b)** neutral (**N**) species of nitroharmines **8 – 10** (isovalue = 0.02 $e^{1/2}$ bohr$^{-3/2}$). HOMO-LUMO and HOMO–1-LUMO are the main transitions involved in the low energy absorption bands (300 nm < λ < 500 nm) of the compounds in H$_2$O. The vertical transition energies were calculated for the optimized ground-state geometry using TD-DFT calculations. All calculations are performed in water at the B3LYP/aug-cc-pVDZ level of theory using the polarizable continuum model.

20.   Other molecular orbital diagram of compounds 5 to 10
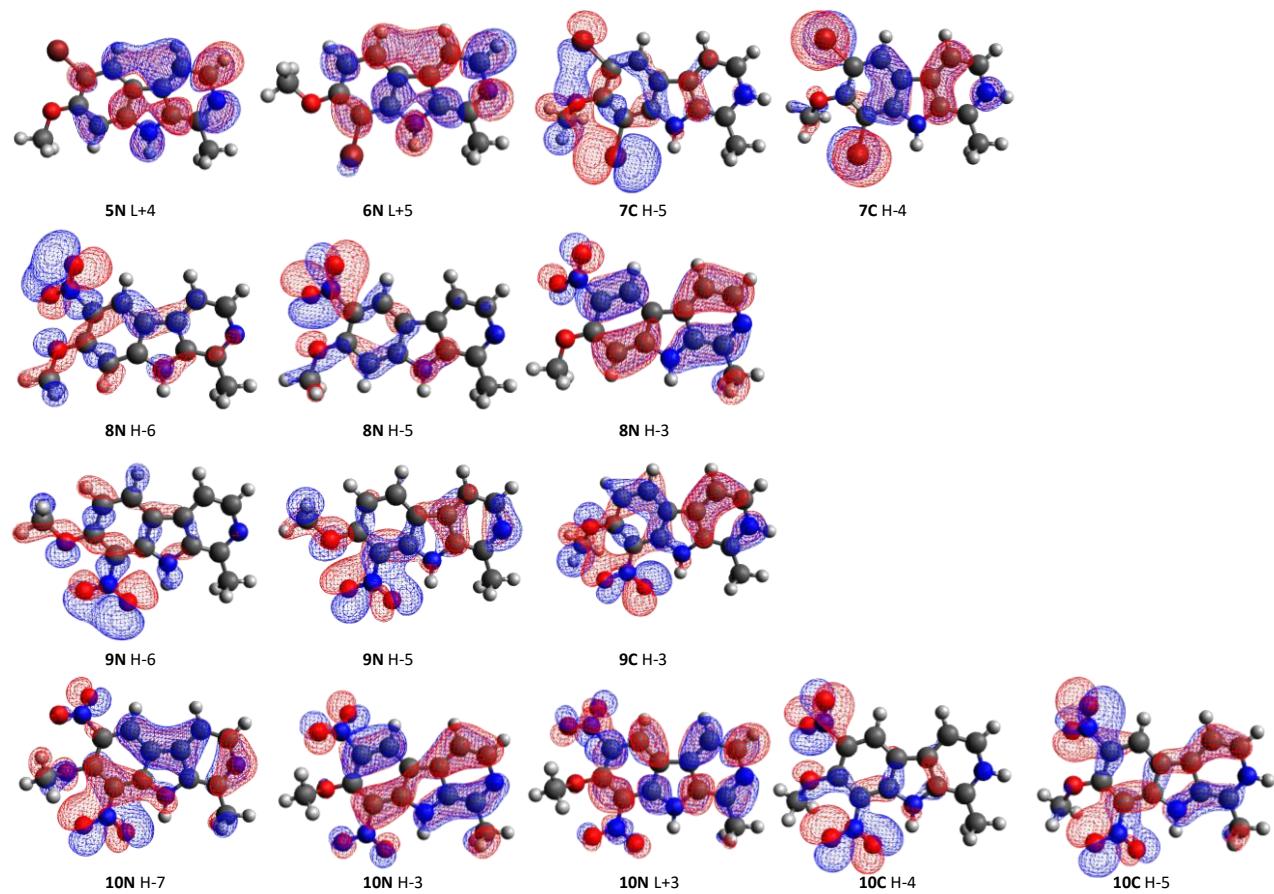
Figure SI.8. Molecular orbital diagram of compounds **5** to **10** (isovalue = 0.02 e$^{1/2}$ bohr$^{-3/2}$) involved in higher energy absorption bands (230 nm > λ > 300 nm) of the compounds in H_2O. The vertical transition energies were calculated at the optimized ground-state geometry using TD-DFT calculations. All calculations are performed in water at the B3LYP/aug-cc-pVDZ level of theory using the polarizable continuum model.

Table SI.13. Self-Consistent Field (E) energies of different tautomeric species calculated at the B3LYP/aug-cc-pVDZ/PCM(water) level of theory. ΔE is the difference of energy between the neutral (**N**) and zwitterionic (**Z**) species (*i.e.*, E(**N**)-E(**Z**)) expressed in eV.

Compound	E / eV	Tautomer	E / eV	ΔE = E(N)-E(Z) / eV
5N	-3260.9942	**5Z**	-3260.9816	-0.3420
6N	-3260.9932	**6Z**	-3260.9764	-0.4594
7N	-5834.5399	**7Z**	-5834.5292	-0.2932
8N	-891.9782	**8Z**	-891.9677	-0.2855
9N	-891.9776	**9Z**	-891.9562	-0.5823
10N	-1096.5004	**10Z**	-1096.4901	-0.2593

22.   Fluorescence spectra of 6-bromoharmine (5) as a function of pH and O₂ concentration.
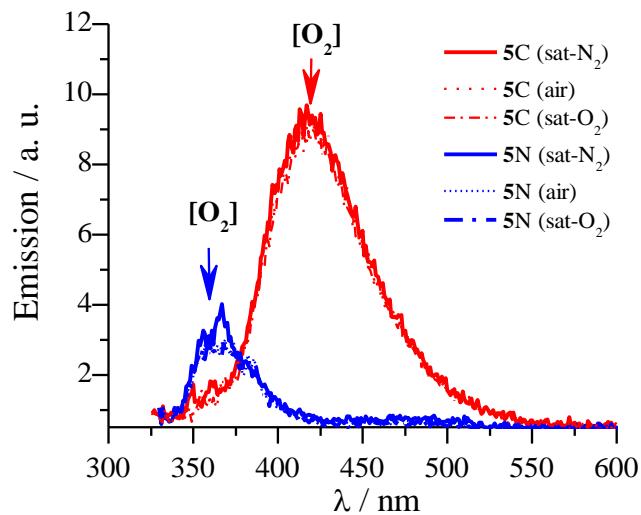
Figure SI.9. Corrected fluorescence spectra of 6-bromoharmine (**5**) in aqueous solution as a function of pH and O_2 concentration. Spectra were obtained for three oxygen concentrations (*i.e.*, N_2-saturated, aerated, and O_2-saturated) under acidic (**red lines**) and alkaline (**blue lines**) conditions. The excitation wavelengths were 325 and 340 nm for acidic and alkaline experiments, respectively.

23. Phosphorescence spectra at 77 K
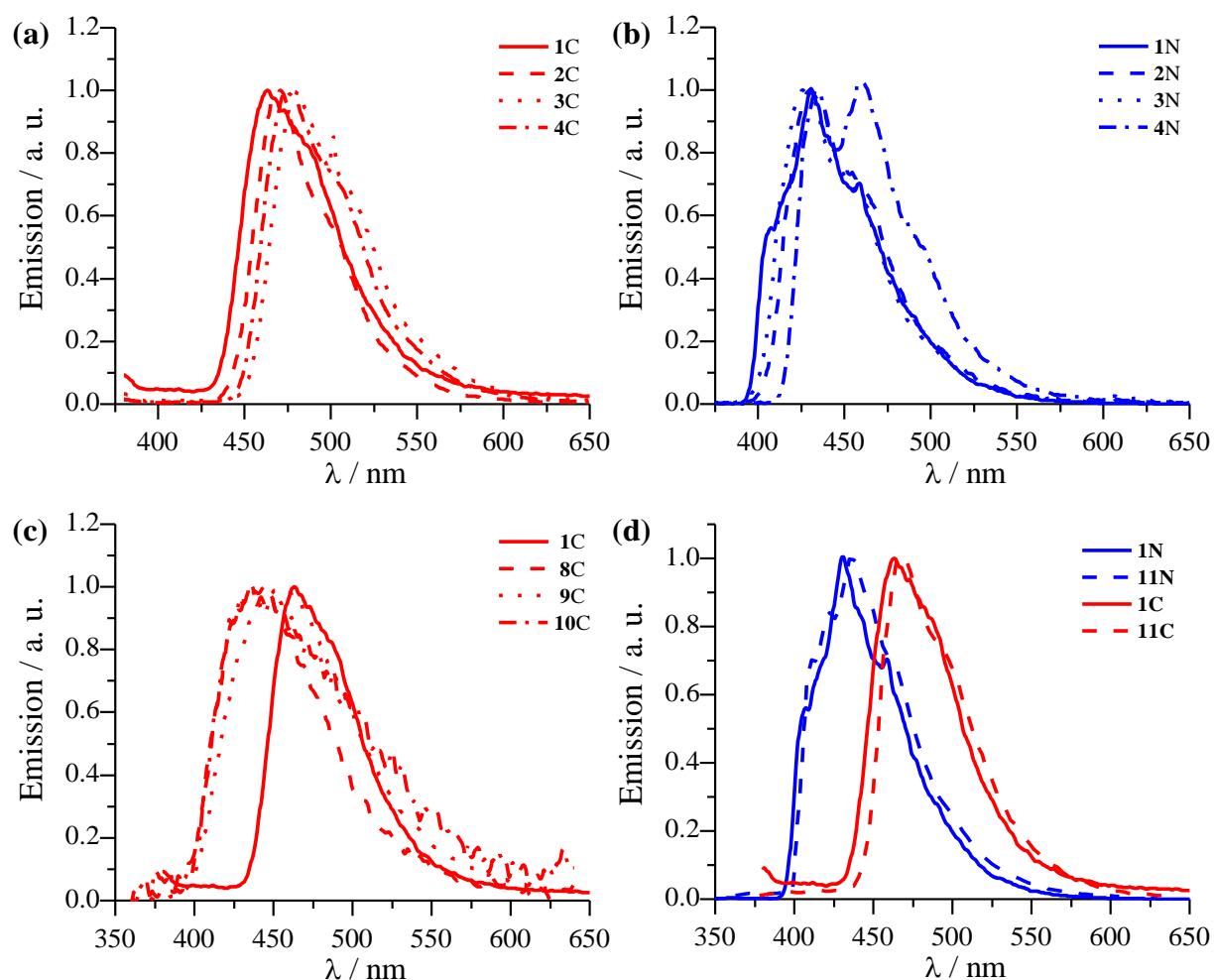
Figure SI.10. Phosphorescence spectra of compounds **(a) 1C–4C**, **(b) 1N–4N**, **(c) 1C** and **8C–10C** and **(d) 11N** and **11C**, measured in solid matrix (isopropanol-ethyl ether (1:1)) at 77 K. For acidic measurements, samples were doped with $HClO_4$ before freezing.

24.   Calculated (0K) vs. experimental (77K) maximum wavelength of phosphoresce emission
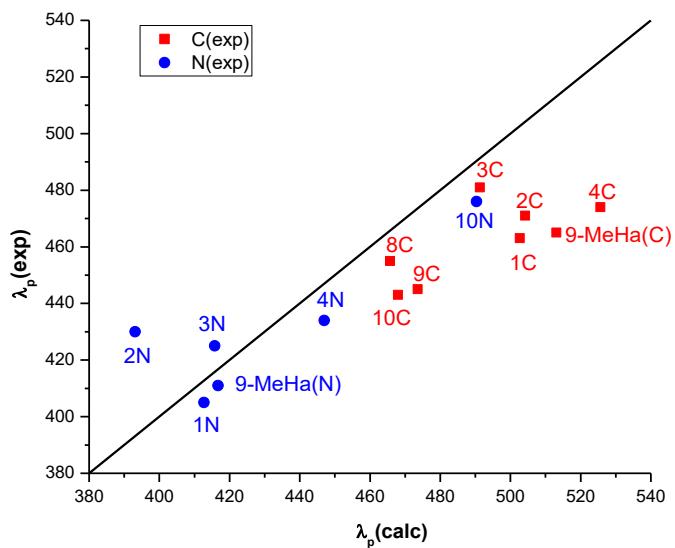
Figure SI.11. Correlation between experimental (measured at 77K) and theoretical (calculated at 0K) maximum wavelength of phosphorescence emission of cationic (**C**) and neutral (**N**) species of compounds **1 – 10** and 9-mehtyl-harmine (9-Me-Ha).

25.   Spin-density distribution of 1 - 3

(a)

(b)

(c)
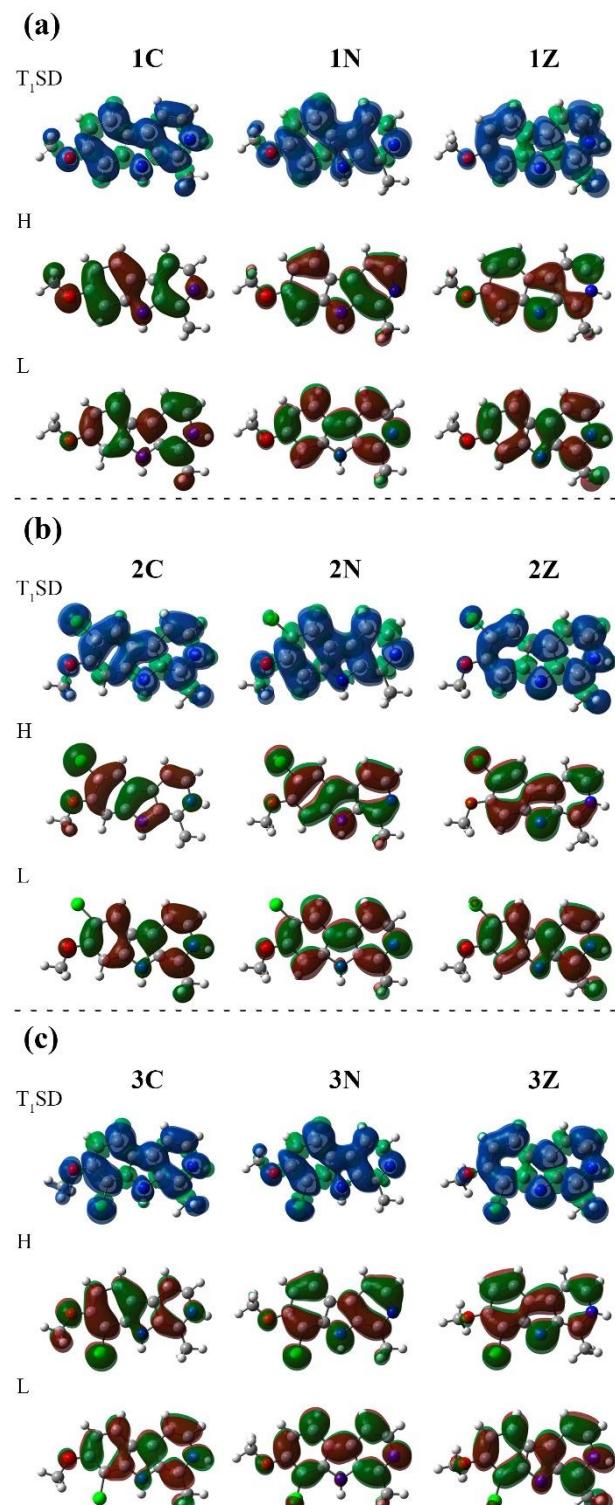
Figure SI.12. *Top*: spin-density distribution (SD) for the fully-relaxed lowest triplet excited states of cationic (**C**), neutral (**N**) and zwitterionic (**Z**) species of harmine (**1**), 6-chloroharmine (**2**) and 8-chloroharmine (**3**); isovalue: 0.0004 e bohr^{-3}. *Bottom*: contour plots of the HOMO and LUMO of all the compounds in their optimized ground-state geometries; isovalue = 0.02 e$^{1/2}$ bohr$^{-3/2}$. All calculations are performed in vacuo at the B3LYP/TZVP level of theory.

26.   Spin-density distribution of 5 - 10
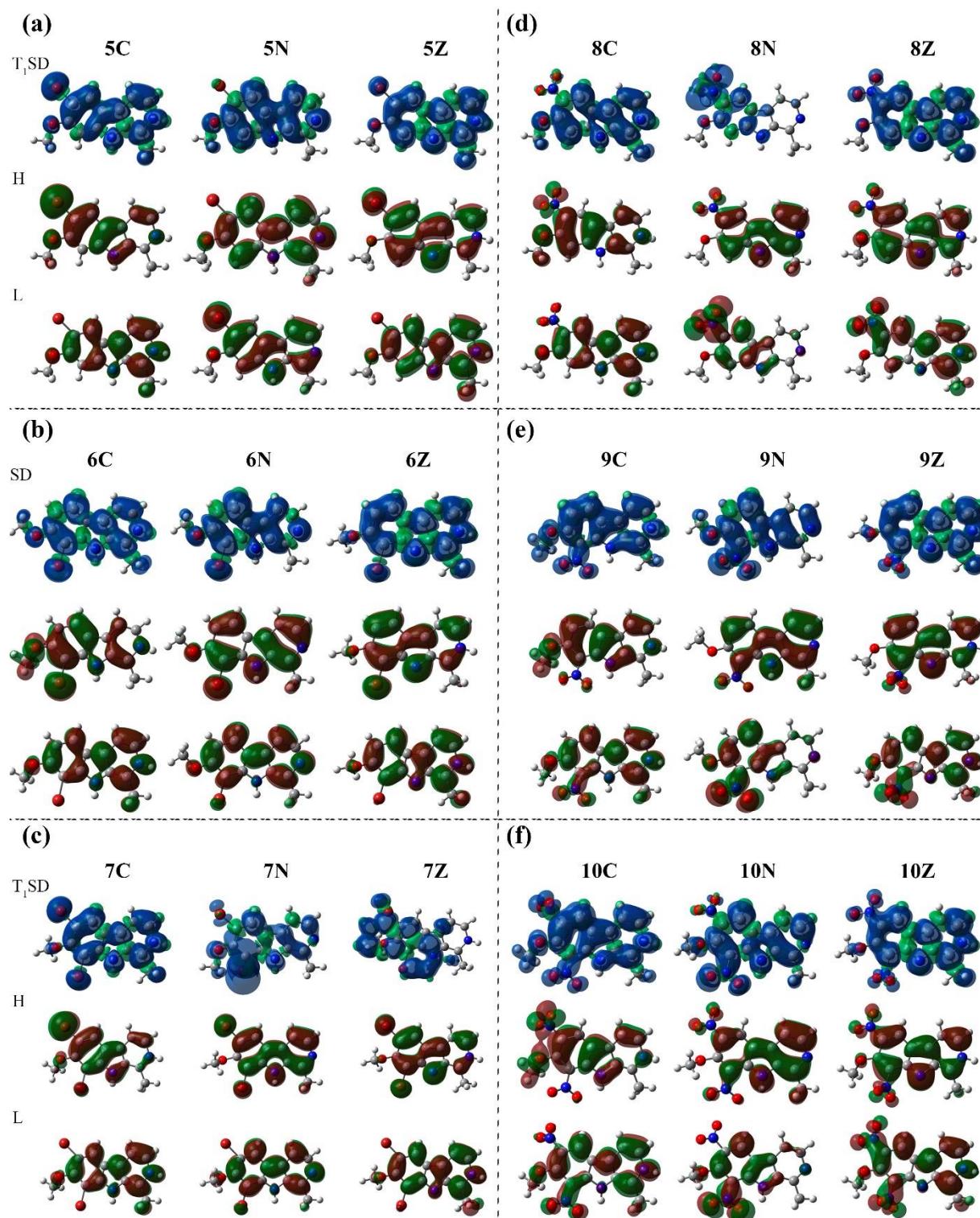
Figure SI.13. *Top*: spin-density distribution (SD) for the fully-relaxed lowest triplet excited states of cationic, neutral and zwitterionic species of compounds **5 - 10**; isovalue: 0.0004 e bohr^{-3}. *Bottom*: Contour plots of the HOMO and LUMO of all the compounds in their optimized ground-state geometries; isovalue = 0.02 e$^{1/2}$ bohr$^{-3/2}$. All calculations are performed in vacuo at the B3LYP/TZVP level of theory.

**27.** **Dipole moments and the total electron density in the ground (S$_0$) and triplet (T$_1$) states**
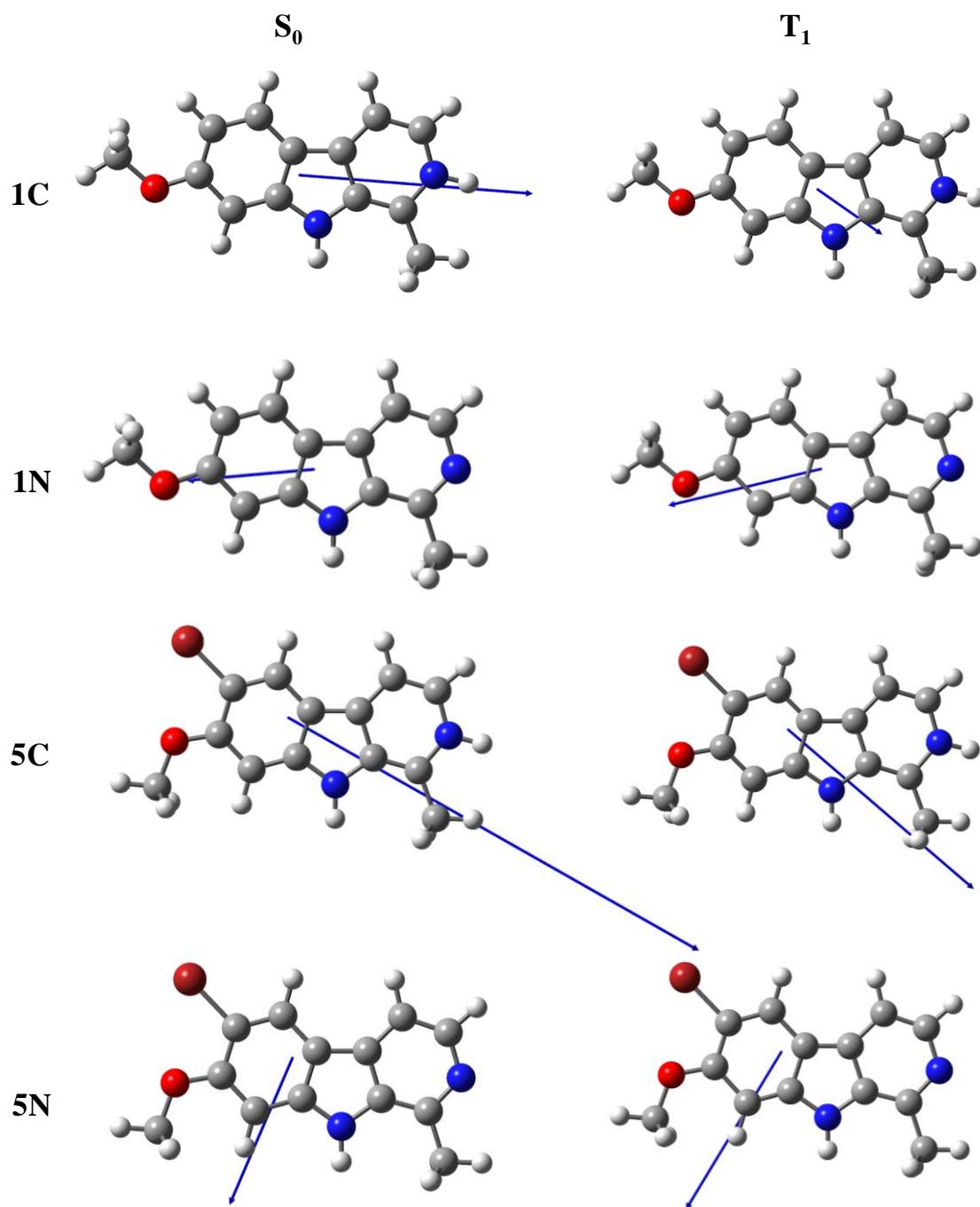
Figure SI.14. ρ and μ plots for singlet ground (S$_0$) and excited triplet (T$_1$) states of cationic (**C**) and neutral (**N**) species of harmine (**1**), and 6-bromoharmine (**5**), as representative examples.

28. **Relationship between λ_{0-0}, $\mu_d^C(T_1)$ and experimental $\Phi_\Delta^{(O_2)}$**
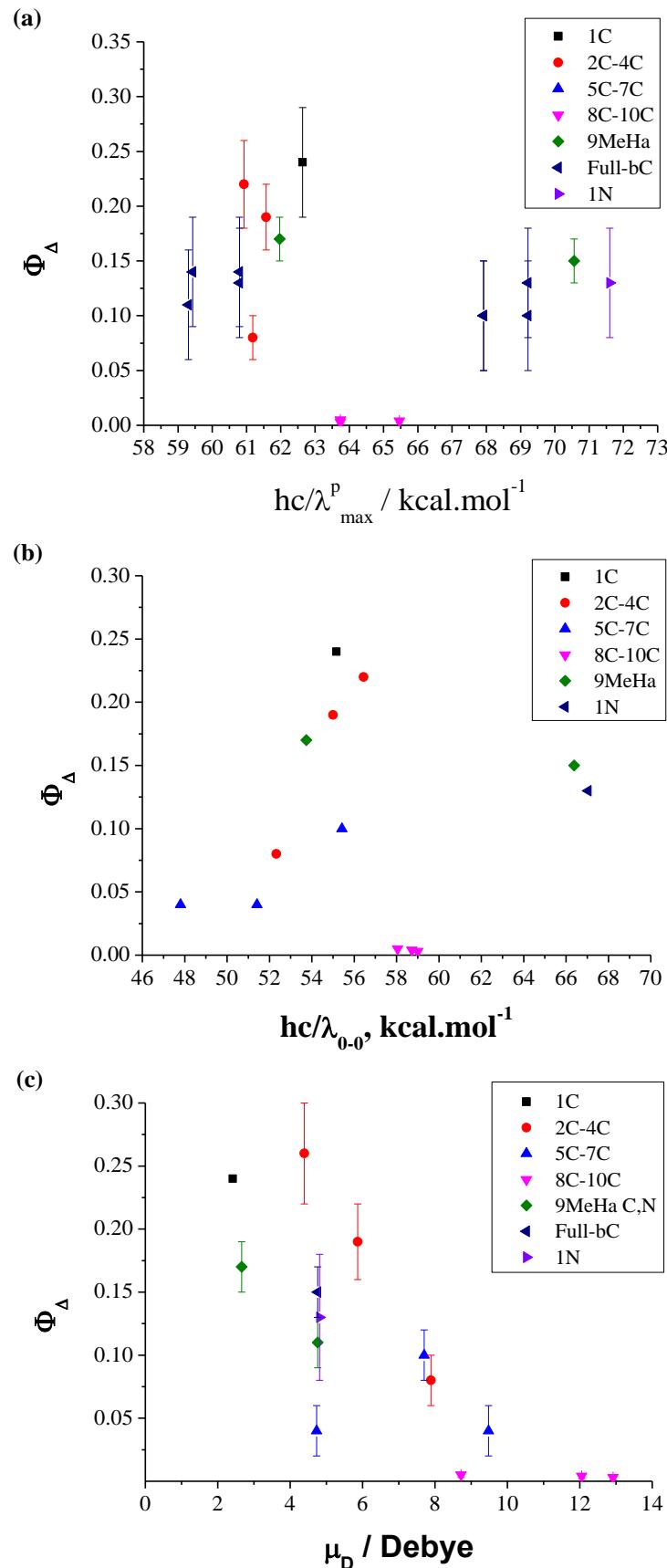

Figure SI.15. Relationship between experimental quantum yield of singlet oxygen production ($\Phi_\Delta^{(O_2)}$) and **(a)** experimental maximum of phosphorescence emission (λ_p^{exp}), **(b)** theoretical λ_{0-0}, and **(c)** theoretical dipole moment in the triplet state ($\mu_d^C(T_1)$) values, respectively.