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

An unusual deprotonation trend in 2-(2'-hydroxyphenyl)pyrido imidazoles

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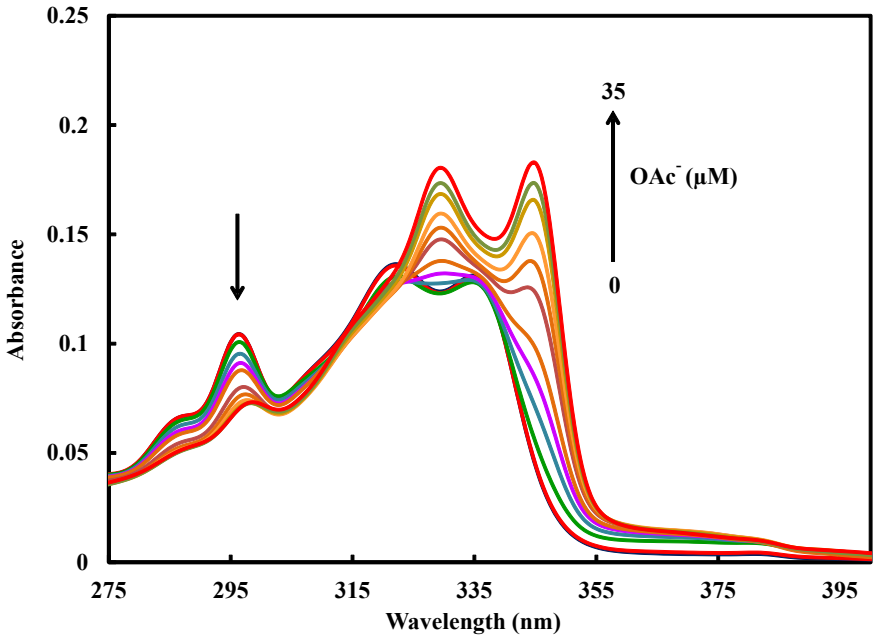


Fig. S1 Absorption spectra of HPIP-b at different acetate concentration.

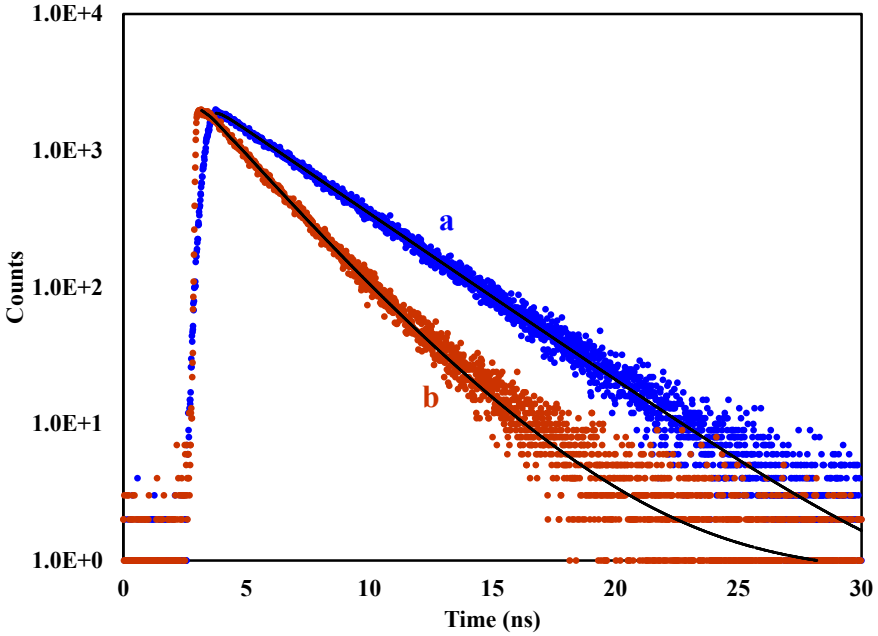


Fig. S2 Fluorescence decay of HPIP-b in presence of fluoride; (a) emission monitored at 455 nm, (b) emission monitored at 410 nm, λ_{ex} = 336 nm.

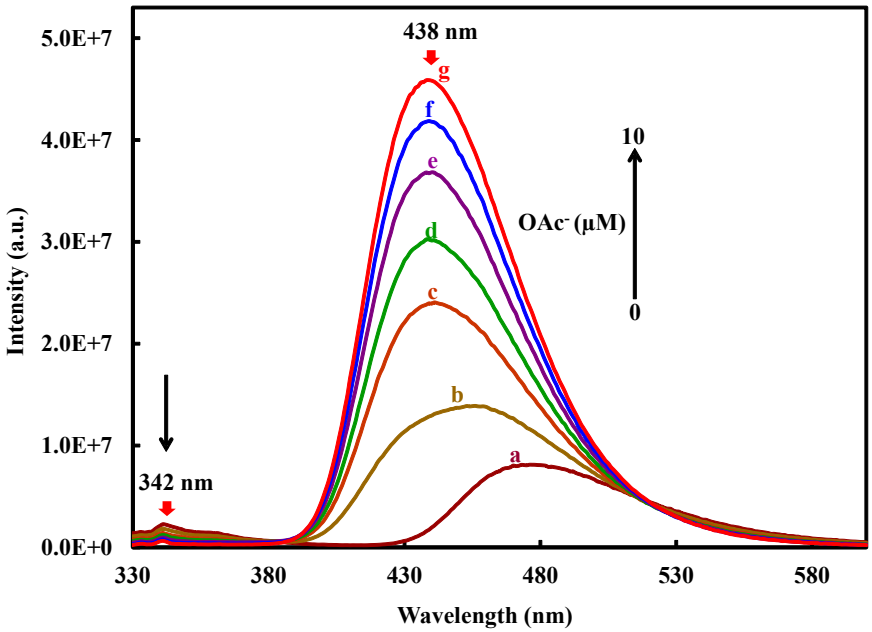


Fig. S3 Emission spectra of HPIP-c at different acetate concentration, (a) 0 μM, (b) 0.4 μM, (c) 0.8 μM, (d) 1.2 μM, (e) 1.8 μM, (d) 3.6 μM, (e) 10 μM. λ_{ex} = 320 nm.

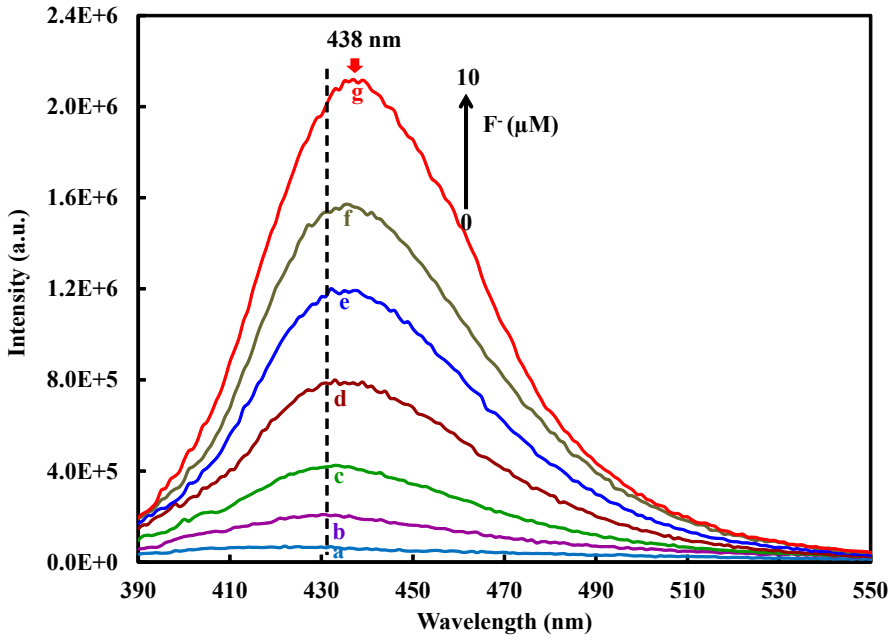


Fig. S4 Emission spectra of HPIP-c at different fluoride concentration, (a) 0 μM, (b) 3.9 μM, (c) 4.8 μM, (d) 6.4 μM, (e) 7.6 μM, (f) 9.3 μM, (h) 10.4 μM. λ_{ex} = 370 nm.

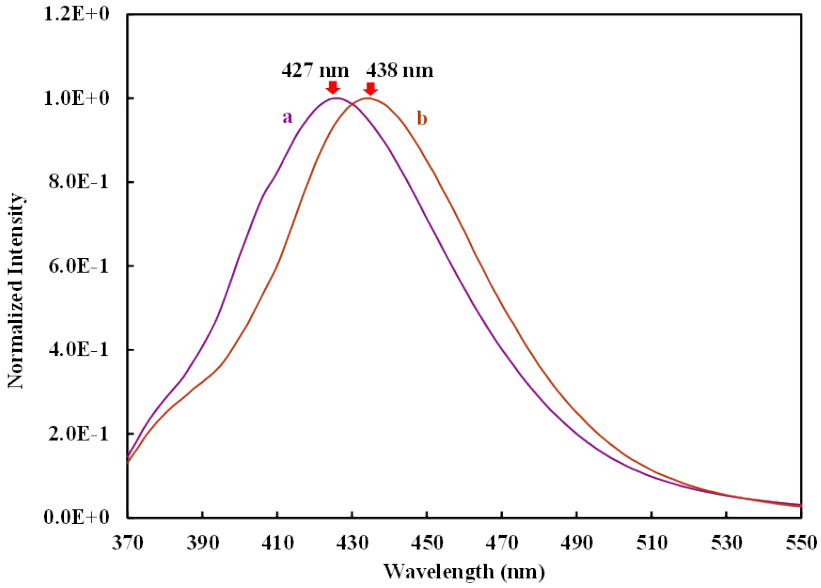


Fig. S5 Normalized emission spectra of HPIP-c at different acetate concentration, (a) 0.8 μM, (b) 10 μM. λ_{ex} = 320 nm.

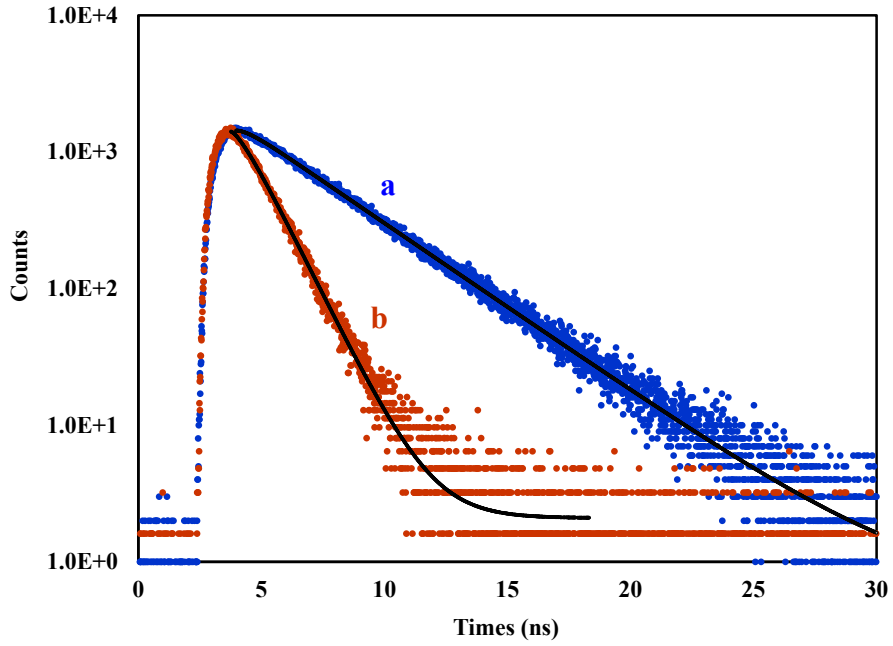


Fig. S6 Fluorescence decay of HPIP-c in presence of fluoride; (a) emission monitored at 455 nm, (b) emission monitored at 390 nm, λ_{ex} = 336 nm.

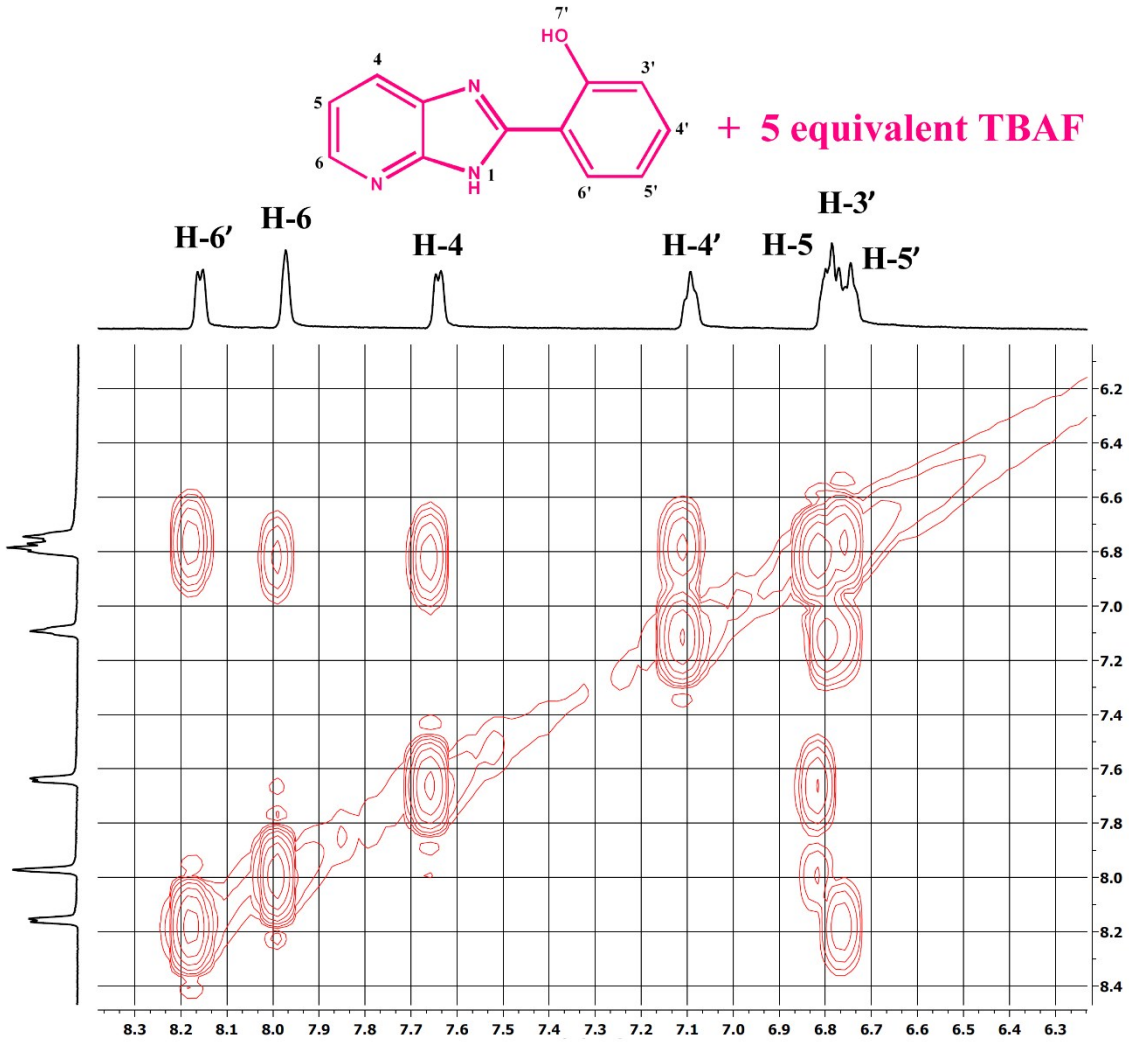


Fig. S7 2D NMR of HPIP-b in presence of 5 equivalent of TBAF.

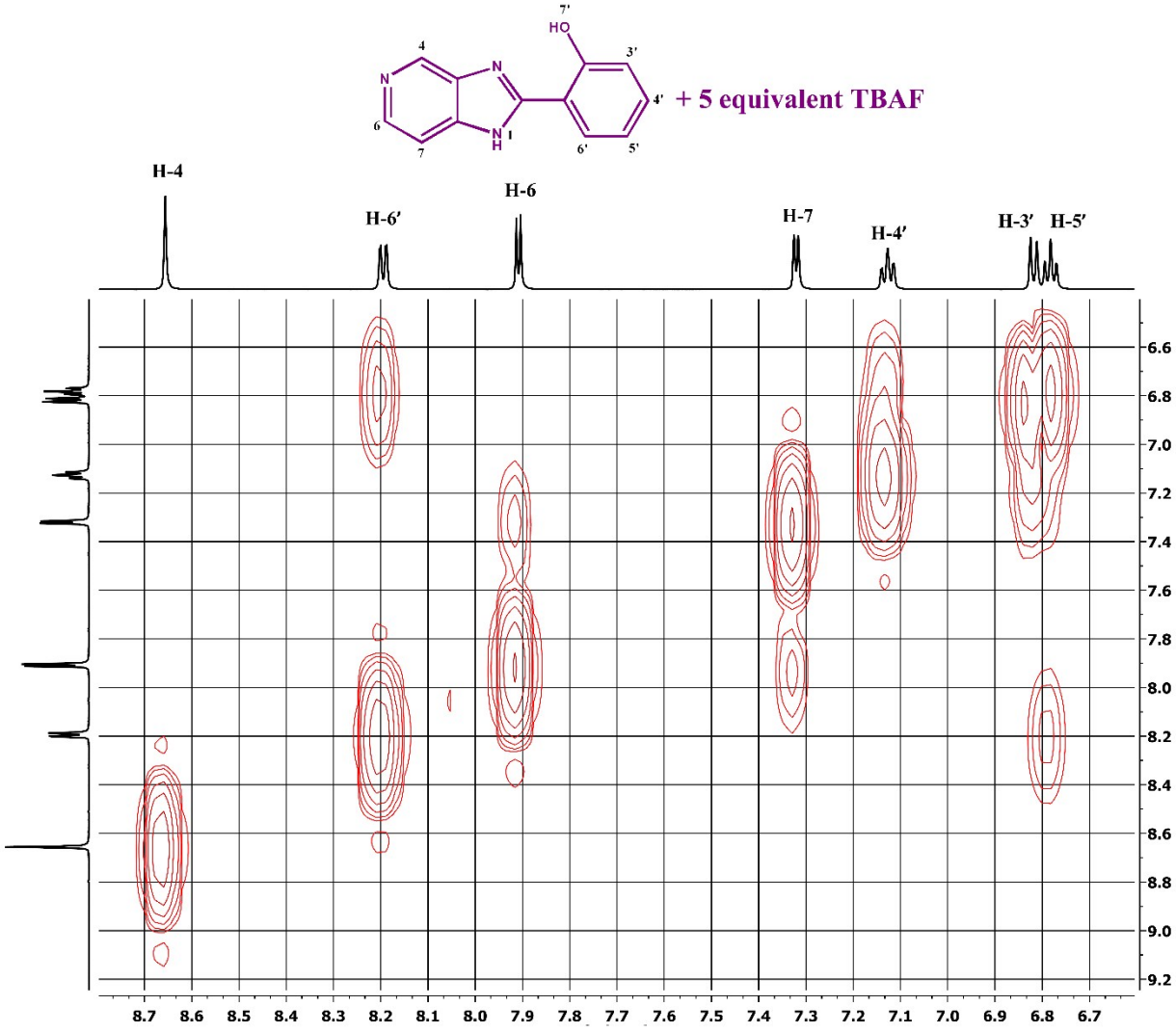


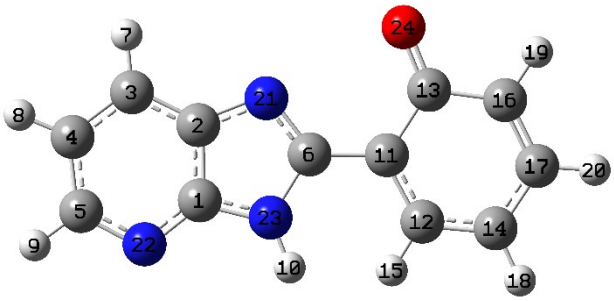
Fig. S8 2D NMR of HPIP-c in presence of 5 equivalent of TBAF.

Table S1 Dihedral angle (ϕ) between the imidazo ring and phenoxide ring for different anions of HPBI, HPIP-b and HPIP-c.

Anion	φ
HPBI cis-anion	43.225[a]
HPBI trans-anion	179.992
HPIP-b cis-anion	-0.006
HPIP-b trans-anion	179.986
HPIP-c cis-anion	-0.055
HPIP-c trans-anion	-179.994

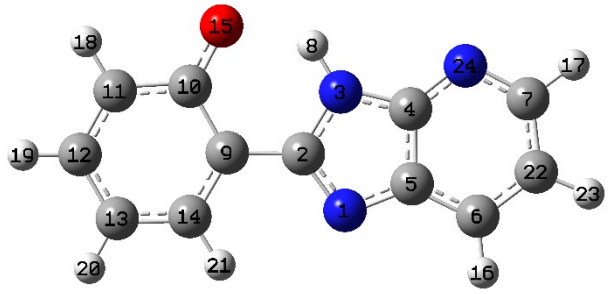
[a] Reference 20 in main article.

Table S2 Ground state optimized Cis- HPIP-b anion and its XYZ coordinates.



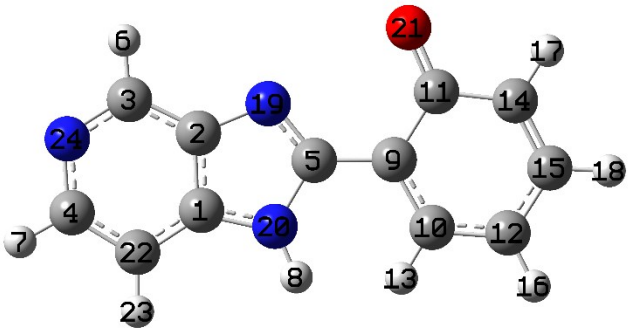
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.01711	-0.73095	-3.8E-05
2	6	-1.95185	0.686589	0.00005
3	6	-3.16006	1.385911	0.000093
4	6	-4.33177	0.617899	0.000045
5	6	-4.26372	-0.78419	-4.3E-05
6	6	0.106962	-0.00161	0.000007
7	1	-3.19003	2.471545	0.000161
8	1	-5.30492	1.098385	0.000076
9	1	-5.17829	-1.37153	-8.1E-05
10	1	-0.4074	-2.10316	-0.00014
11	6	1.561396	-0.11097	0.000008
12	6	2.146446	-1.40333	0.000054
13	6	2.435378	1.063086	-3.8E-05
14	6	3.516017	-1.62084	0.000059
15	1	1.511598	-2.28512	0.000099
16	6	3.854689	0.777385	-2.8E-05
17	6	4.375394	-0.50098	0.000018
18	1	3.911881	-2.6316	0.000099
19	1	4.515536	1.641453	-0.00006
20	1	5.454238	-0.64503	0.000023
21	7	-0.63811	1.107547	0.000074
22	7	-3.11135	-1.48712	-8.7E-05
23	7	-0.70591	-1.1402	-6.4E-05
24	8	2.030548	2.274414	-9.5E-05

Table S3 Ground state optimized trans-HPIP-b anion and its XYZ coordinates.



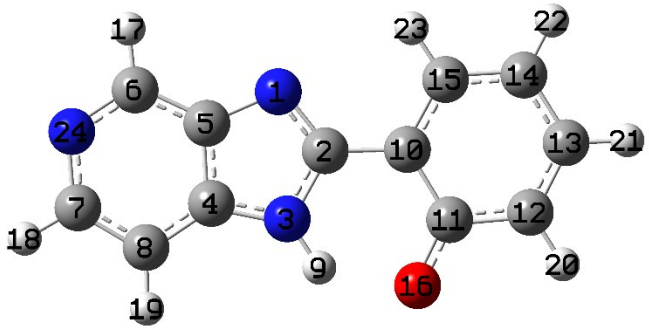
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.677149	-1.35091	0.00004
2	6	-0.1171	-0.2725	-0.00009
3	7	0.595705	0.906359	-0.00037
4	6	1.929576	0.583261	-0.00017
5	6	1.95985	-0.8434	0.000039
6	6	3.213398	-1.45994	0.000187
7	6	4.171639	0.778531	-0.00014
8	1	0.064624	1.791193	-0.00068
9	6	-1.57067	-0.25121	-0.00009
10	6	-2.27934	1.014805	0.000073
11	6	-3.71119	0.927736	0.000242
12	6	-4.38105	-0.28601	0.000065
13	6	-3.67175	-1.50535	-0.00017
14	6	-2.28299	-1.46834	-0.0002
15	8	-1.67761	2.164175	0.000687
16	1	3.31664	-2.54128	0.00036
17	1	5.046795	1.423481	-0.00022
18	1	-4.26332	1.864691	0.000528
19	1	-5.46922	-0.29584	0.000165
20	1	-4.19965	-2.4542	-0.00027
21	1	-1.71224	-2.39292	-0.00033
22	6	4.331153	-0.61712	0.000095
23	1	5.33369	-1.03311	0.000197
24	7	2.97777	1.404801	-0.00029

Table S4 Ground state optimized cis-HPIP-c anion and its XYZ coordinates.



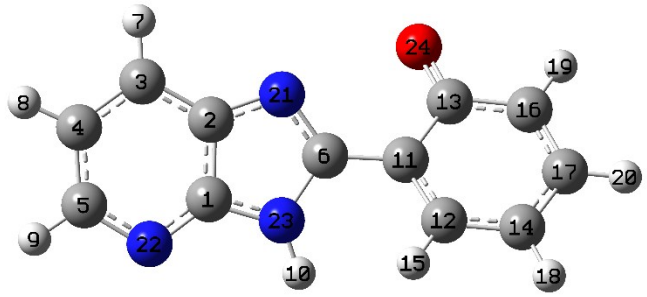
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.00346	-0.76541	-0.0003
2	6	-1.94934	0.648189	0.000429
3	6	-3.15454	1.358343	0.000803
4	6	-4.36079	-0.62114	-0.00026
5	6	0.115845	-0.01315	0.000094
6	1	-3.16367	2.446315	0.001373
7	1	-5.34699	-1.07904	-0.00051
8	1	-0.37507	-2.11758	-0.00114
9	6	1.571279	-0.11582	0.000102
10	6	2.163561	-1.40457	0.000611
11	6	2.43789	1.063467	-0.00042
12	6	3.534534	-1.61396	0.000597
13	1	1.534397	-2.29046	0.001176
14	6	3.858827	0.786396	-0.00043
15	6	4.386985	-0.489	0.00005
16	1	3.936544	-2.62224	0.001035
17	1	4.514712	1.654203	-0.00084
18	1	5.466664	-0.62669	0.000028
19	7	-0.63834	1.085581	0.000647
20	7	-0.6918	-1.16072	-0.0005
21	8	2.025043	2.271858	-0.00097
22	6	-3.22661	-1.43618	-0.00068
23	1	-3.31032	-2.51795	-0.00125
24	7	-4.34154	0.731655	0.000465

Table S5 Ground state optimized trans-HPIP-c anion and its XYZ coordinates.



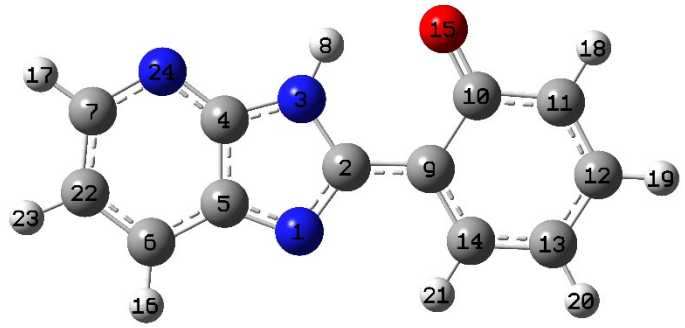
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.677827	-1.33219	-9E-06
2	6	-0.12515	-0.26461	-6E-06
3	7	0.580928	0.922458	0.000193
4	6	1.914322	0.61319	0.000106
5	6	1.956957	-0.80787	-5.3E-05
6	6	3.209791	-1.43257	-0.00017
7	6	4.279174	0.62563	0.000044
8	6	3.092974	1.361083	0.000157
9	1	0.035777	1.800067	0.000376
10	6	-1.57946	-0.24943	-2.2E-05
11	6	-2.29197	1.013856	-0.00015
12	6	-3.72318	0.922501	-5.3E-05
13	6	-4.38911	-0.29351	0.00006
14	6	-3.67599	-1.51045	0.000099
15	6	-2.28726	-1.46899	0.000064
16	8	-1.69363	2.165807	-0.00022
17	1	3.295137	-2.51754	-0.00026
18	1	5.232819	1.148031	0.000082
19	1	3.103365	2.446083	0.000283
20	1	-4.27828	1.857676	-9.3E-05
21	1	-5.47722	-0.30682	0.000099
22	1	-4.20085	-2.46095	0.000177
23	1	-1.71355	-2.39178	0.000126
24	7	4.35056	-0.72659	-0.00011

Table S6 Excited state optimized cis-HPIP-b anion and its XYZ coordinates.



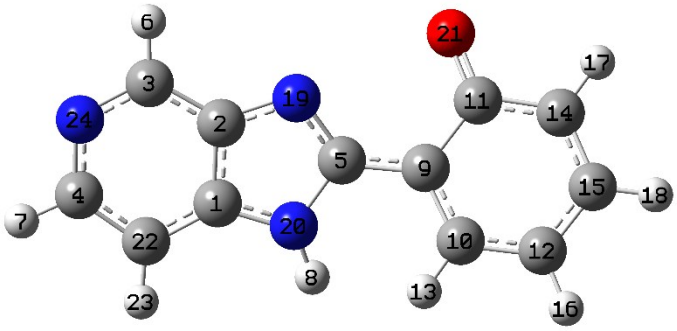
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.01792	-0.69613	-0.19896
2	6	-1.94679	0.655542	0.245888
3	6	-3.17311	1.335631	0.4827
4	6	-4.33983	0.579726	0.247608
5	6	-4.27888	-0.7437	-0.19681
6	6	0.110952	0.007331	-0.03505
7	1	-3.20653	2.368774	0.812068
8	1	-5.31824	1.027112	0.40481
9	1	-5.19592	-1.29972	-0.37504
10	1	-0.40842	-1.96397	-0.73913
11	6	1.555123	-0.1311	0.033944
12	6	2.140691	-1.36953	0.325292
13	6	2.452825	1.013881	-0.22154
14	6	3.54047	-1.54923	0.36113
15	1	1.506629	-2.22253	0.548711
16	6	3.871818	0.790384	-0.12101
17	6	4.407251	-0.46699	0.147636
18	1	3.941727	-2.53613	0.570693
19	1	4.512478	1.645005	-0.31853
20	1	5.482788	-0.61134	0.187086
21	7	-0.64578	1.060042	0.344863
22	7	-3.111	-1.42919	-0.44486
23	7	-0.70954	-1.08692	-0.33875
24	8	2.001768	2.153796	-0.55557

Table S7 Excited state optimized trans-HPIP-b anion and its XYZ coordinates.



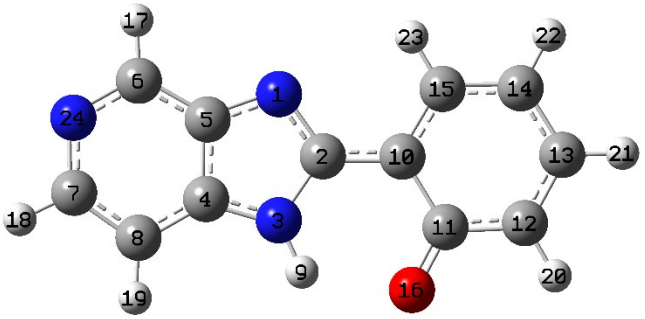
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-0.68485	-1.30383	0.000018
2	6	0.120287	-0.20819	0.000114
3	7	-0.64463	0.954323	0.000203
4	6	-1.96365	0.60211	0.000086
5	6	-1.96324	-0.82836	-9E-06
6	6	-3.21887	-1.48723	-0.00011
7	6	-4.21965	0.748679	-6E-06
8	1	-0.21899	1.875161	0.000312
9	6	1.556879	-0.23896	0.000159
10	6	2.353752	1.007365	0.000228
11	6	3.783795	0.897219	-0.00021
12	6	4.424829	-0.34094	-0.00019
13	6	3.651928	-1.519	0.000069
14	6	2.248309	-1.46642	0.00017
15	8	1.779687	2.150004	-0.00034
16	1	-3.30214	-2.56918	-0.00019
17	1	-5.11014	1.372941	0
18	1	4.346409	1.826514	-0.0005
19	1	5.509231	-0.3999	-0.00042
20	1	4.14465	-2.48711	0.000049
21	1	1.673436	-2.38599	0.000248
22	6	-4.34846	-0.64467	-0.00011
23	1	-5.34789	-1.07187	-0.00019
24	7	-3.02589	1.422343	0.000103

Table S8 Excited state optimized cis-HPIP-c anion and its XYZ coordinates.



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.00194	-0.73801	-0.18311
2	6	-1.94128	0.6315	0.204918
3	6	-3.1661	1.317191	0.412235
4	6	-4.37454	-0.59859	-0.1213
5	6	0.124894	-0.00523	-0.04367
6	1	-3.18307	2.365581	0.699909
7	1	-5.36012	-1.04584	-0.2373
8	1	-0.38041	-2.00503	-0.68065
9	6	1.56039	-0.1372	0.025432
10	6	2.159782	-1.38264	0.286937
11	6	2.456524	1.020791	-0.19357
12	6	3.562674	-1.5506	0.316299
13	1	1.536105	-2.24723	0.494299
14	6	3.873269	0.807619	-0.09376
15	6	4.422307	-0.45864	0.136173
16	1	3.970458	-2.54094	0.497475
17	1	4.507565	1.672183	-0.26863
18	1	5.499005	-0.59573	0.170192
19	7	-0.64921	1.057342	0.295388
20	7	-0.69597	-1.12548	-0.29811
21	8	1.993191	2.165776	-0.50186
22	6	-3.22837	-1.38671	-0.36694
23	1	-3.3107	-2.42497	-0.67045
24	7	-4.35626	0.693688	0.250182

Table S9 Excited state optimized trans-HPIP-c anion and its XYZ coordinates.



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.685775	-1.28761	-0.00005
2	6	-0.13192	-0.19657	0.000001
3	7	0.630885	0.975633	0.000024
4	6	1.947207	0.633631	0.000012
5	6	1.95838	-0.79444	-3.1E-05
6	6	3.212397	-1.45134	-5.7E-05
7	6	4.324276	0.592694	0.000007
8	6	3.145844	1.363577	0.000031
9	1	0.188987	1.889073	0.000042
10	6	-1.5625	-0.23519	0.000017
11	6	-2.36943	1.007037	0.000061
12	6	-3.79628	0.893642	0.000023
13	6	-4.4355	-0.35123	-4E-06
14	6	-3.65662	-1.52404	-1.2E-05
15	6	-2.25145	-1.46914	-8E-06
16	8	-1.79587	2.152352	0.00003
17	1	3.279919	-2.5366	-9.3E-05
18	1	5.287541	1.100016	0.000017
19	1	3.178671	2.447748	0.000062
20	1	-4.36182	1.821301	0.000022
21	1	-5.51958	-0.41484	-2.3E-05
22	1	-4.14544	-2.49449	-3.7E-05
23	1	-1.67457	-2.3873	-2.7E-05
24	7	4.372886	-0.75309	-3.6E-05