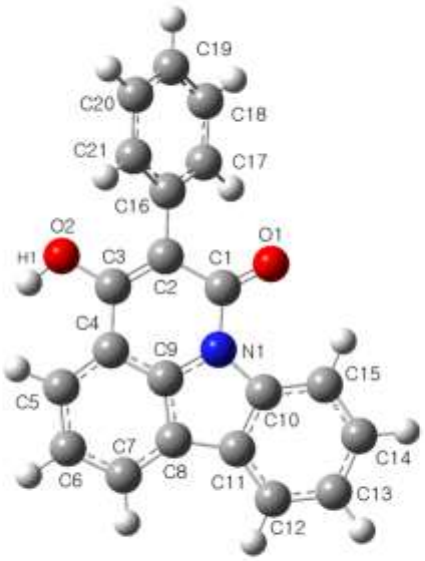

Figure S1. Optimized molecular structure of HPPCO.

Table S1. Selected bond lengths (Å), and bond and dihedral angles (°) of the neutral HPPCO molecule (atomic labeling is shown in Scheme S1).

Definition	Value	Definition	Value	Definition	Value
C1-O1	1.2253	C5-C6	1.3982	C3-O2	1.3584
C1-N1	1.4105	C10-C15	1.3924	C16-C17	1.4051
C1-C2	1.4814	C10-C11	1.4203	C16-C21	1.4045
N1-C9	1.3744	C15-17	1.0814	C17-C18	1.3932
C9-C8	1.4069	C2-C3	1.3788	C21-C20	1.3936
C9-C4	1.3921	C2-C16	1.4875	O2-H1	0.9659
C8-C7	1.3947	C4-C3	1.4518	C7-C6	1.4036
C4-C5	1.4077				
0O1-C1-N1	120.1822	C9-C8-C11	105.5465	C1-C2-C16	117.0499
O1-C1-C2	124.8608	C7-C8-C11	136.7237	C3-C2-C16	121.7537
N1-C1-C2	114.9557	C9-C4-C5	115.8381	C4-C3-C2	121.6819
C1-N1-C9	122.5948	C9-C4-C3	115.7458	C4-C3-O2	119.1379
C1-N1-C10	129.4874	C5-C4-C3	128.4162	C2-C3-O2	119.18
C9-N1-C10	107.9165	C8-C7-C6	118.844	C2-C16-C17	120.757
N1-C9-C8	111.1303	C4-C5-C6	120.5956	C2-C16-C21	120.906
N1-C9-C4	123.8097	C7-C6-C5	121.9301	C17-C16-C21	118.3362
C8-C9-C4	125.0599	C1-C2-C3	121.1942	C3-O2-H1	109.635
C9-C8-C7	117.7296				
O1-C1-N1-C9	-179.861	C4-C9-C8-C11	-179.95	C4-C5-C6-C7	0.2992
O1-C1-N1-C10	0.5926	N1-C9-C4-C5	-179.394	N1-C10-C11-C8	-0.0697
C2-C1-N1-C9	-0.2585	N1-C9-C4-C3	0.5728	C1-C2-C3-C4	1.5591
C2-C1-N1-C10	-179.805	C8-C9-C4-C5	0.5001	C1-C2-C3-O2	-178.282
O1-C1-C2-C3	178.9272	C8-C9-C4-C3	-179.533	C16-C2-C3-C4	-179.01
O1-C1-C2-C16	-0.5298	C9-C8-C7-C6	-0.237	C16-C2-C3-O2	1.1491
N1-C1-C2-C3	-0.6541	C11-C8-C7-C6	179.5656	C1-C2-C16-C17	46.7686
N1-C1-C2-C16	179.8889	C9-C8-C11-C10	0.0687	C1-C2-C16-C21	-132.895
C1-N1-C9-C8	-179.631	C7-C8-C11-C10	-179.75	C3-C2-C16-C17	-132.685
C1-N1-C9-C4	0.2764	C9-C4-C5-C6	-0.5887	C3-C2-C16-C21	47.6516
C10-N1-C9-C8	0.001	C3-C4-C5-C6	179.449	C4-C3-O2-H1	-9.7512
C10-N1-C9-C4	179.9084	C9-C4-C3-C2	-1.4842	C2-C3-O2-H1	170.0942
C1-N1-C10-C11	179.642	C9-C4-C3-O2	178.3572	C2-C16-C17-C18	179.6126
C9-N1-C10-C11	0.0437	C5-C4-C3-C2	178.478	C21-C16-C17-C18	-0.7157
N1-C9-C8-C7	179.8161	C5-C4-C3-O2	-1.6806	C2-C16-C21-C20	-179.873
N1-C9-C8-C11	-0.0435	C8-C7-C6-C5	0.1349	C17-C16-C21-C20	0.4556
C4-C9-C8-C7	-0.0899				

Table S2. Selected bond lengths (Å) and bond angles (°) of the deprotonated HPPCO molecule.

Definition	Value	Definition	Value	Definition	Value
C1-O1	1.2415	C8-C7	1.3995	C2-C3	1.4525
C1-N1	1.4421	C4-C5	1.3975	C2-C16	1.4848
C1-C2	1.4463	C4-C3	1.493	C3-O2	1.2515
C3-C9	1.3728	C7-C6	1.4014	C16-C17	1.4145
C9-C8	1.4087	C5-C6	1.4047	C16-C21	1.4146
C9-C4	1.3867				
O1-C1-N1	116.0646	C9-C4-C3	118.9204	C3-C2-C16	119.3329
O1-C1-C2	127.9695	C5-C4-C3	125.0747	C4-C3-C2	116.4548
N1-C1-C2	115.9636	C8-C7-C6	118.6626	C4-C3-O2	117.4425
C1-N1-C9	122.2893	C4-C5-C6	120.7815	C2-C3-O2	126.1006
N1-C9-C4	123.3996	C7-C6-C5	121.7798	C2-C16-C17	122.2343
C8-C9-C4	125.1628	C1-C2-C3	122.9565	C2-C16-C21	121.4091
C9-C8-C7	117.6093	C1-C2-C16	117.7105	C17-C16-C21	116.3543
C9-C4-C5	116.004				
O1-C1-N1-C9	179.8385	C4-C9-C8-C7	0.0803	C8-C7-C6-C5	-0.0882
O1-C1-N1-C10	-0.6805	C4-C9-C8-C11	-179.93	C4-C5-C6-C7	0.1316
C2-C1-N1-C9	0.3433	N1-C9-C4-C5	179.9703	N1-C10-C11-C8	-0.0089
C2-C1-N1-C10	179.8243	N1-C9-C4-C3	-0.3473	C1-C2-C3-C4	-1.4393
O1-C1-C2-C3	-178.76	C8-C9-C4-C5	-0.0399	C1-C2-C3-O2	179.1093
O1-C1-C2-C16	1.1406	C8-C9-C4-C3	179.6425	C16-C2-C3-C4	178.6621
N1-C1-C2-C3	0.6653	C9-C8-C7-C6	-0.0138	C16-C2-C3-O2	-0.7893
N1-C1-C2-C16	-179.435	C11-C8-C7-C6	-180	C1-C2-C16-C17	28.9722
C1-N1-C9-C8	179.5128	C9-C8-C11-C10	-0.0306	C1-C2-C16-C21	-151.594
C1-N1-C9-C4	-0.4962	C7-C8-C11-C10	179.9567	C3-C2-C16-C17	-151.124
C10-N1-C9-C8	-0.0684	C9-C4-C5-C6	-0.0656	C3-C2-C16-C21	28.31
C10-N1-C9-C4	179.9227	C3-C4-C5-C6	-179.726	C2-C16-C17-C18	179.5485
C1-N1-C10-C11	-179.493	C9-C4-C3-C2	1.2595	C21-C16-C17-C18	0.0876
C9-N1-C10-C11	0.0464	C9-C4-C3-O2	-179.24	C2-C16-C21-C20	-179.741
N1-C9-C8-C7	-179.929	C5-C4-C3-C2	-179.089	C17-C16-C21-C20	-0.2751
N1-C9-C8-C11	0.0614	C5-C4-C3-O2	0.4112		

Table S3. Some DFT molecular orbitals calculated for neutral HPPCO molecule.

MO	hartree	% contribution from each part of the compound															
		15C				6C				N				2O			
		s	p_x	p_y	p_z	s	p_x	p_y	p_z	s	p_x	p_y	p_z	s	p_x	p_y	p_z
*l*8	0.067	0	0	0	94	0	0	1	1	0	0	0	1	0	0	0	2
*l*7	0.034	0	0	0	12	0	4	38	44	0	0	0	1	0	0	0	1
*l*6	0.033	0	0	0	19	0	3	34	39	0	0	0	2	0	0	0	1
*l*4	0.022	0	0	0	80	0	1	8	9	0	0	0	1	0	0	0	0
*l*3	0.014	0	0	0	90	0	0	0	0	0	0	0	0	0	0	0	9
*l*2	0.001	0	0	0	91	0	0	2	2	0	0	0	4	0	0	0	0
*l*1	-0.036	0	0	0	88	0	0	2	1	0	0	0	1	0	0	0	7
*h*1	-0.290	0	0	0	52	0	2	15	18	0	0	0	2	0	0	0	11
*h*2	-0.304	0	0	0	98	0	0	0	0	0	0	0	1	0	0	0	0
*h*3	-0.314	0	0	0	67	0	1	5	6	0	0	0	16	0	0	0	4
*h*4	-0.326	0	0	0	0	0	4	43	49	0	0	0	0	0	3	0	0
*h*5	-0.338	0	0	1	50	0	2	21	21	0	0	0	0	0	0	0	3
*h*6	-0.364	0	0	0	84	0	1	4	3	0	0	0	3	0	0	0	5
*h*7	-0.366	1	8	3	0	0	2	2	2	0	1	3	0	0	73	4	0
*h*8	-0.393	0	0	0	81	0	0	1	1	0	0	0	0	0	0	0	16
*h*9	-0.427	0	1	1	43	0	3	1	0	0	0	0	20	0	0	0	29
*h*10	-0.437	1	43	7	3	0	14	5	2	0	0	0	2	1	8	1	1

Table S4. ZINDO electronic states and predominant transitions of neutral HPPCO molecule.

State	nm	f	Predominant transition	comment
(A-absorption)				
1A	361	0.294	*h*1→*l*1	π(R3,4;O;ph)→π*(R1-4)
2A	353	0.104	*h*7→*l*1,*l*3	n(O)→π*(R1-4),π*(R1,3,4)
3A	324	0.235	*h*2→*l*1	π(R1-3)→π*(R1-4)
B-absorption				
4A	311	0.092	*h*3→*l*1	π(R1-4,N)→π*(R1-4)
5A	284	0.016	*h*3→*l*2; *h*2→*l*4	π(R1-4,N)→π*(R1-4); π(R1-3)→π*(R1,3,4)
6A	279	0.006	*h*4→*l*1,*l*5,*l*6; *h*1→*l*6,*l*5	π(ph)→π*(R1-4), π*(R1,2), π*(ph); π(R3,4;O;ph)→π*(ph), π*(R1,2)
7A	274	0.275	*h*3→*l*1; *h*2→*l*2; *h*1→*l*2	π(R1-4,N)→π*(R1-4); π(R1-3)→π*(R1-4); π(R3,4;O;ph)→π*(R1-4)
8A	266	0.352	*h*1→*l*3, *l*2	π(R3,4;O;ph)→π*(R1,3,4)
9A	259	0.363	*h*2→*l*2	π(R1-3)→π*(R1-4)
10A	256	0.001	*h*5→*l*1	π(R1,3,4;ph)→π*(R1-4)
(C-absorption)				
11A	245	0.314	*h*5→ *l*1; *h*1→*l*4	π(R1,3,4;ph)→π*(R1-4); π(R3,4;O;ph)→π*(R1,3,4)
12A	242	0.215	*h*2→*l*3	π(R1-3)→π*(R1,3,4)
13A	240	0.090	*h*4→ *l*1	π(ph)→π*(R1-4)
14A	238	0.011	*h*1→*l*8	π(R3,4;O;ph)→π*(R1-4)
15A	233	0.129	*h*2→*l*3; *h*3→*l*4	π(R1-3)→π*(R1,3,4); π(R1-4,N)→π*(R1-4)
16A	229	0.794	*h*3→*l*2	π(R1-4,N)→π*(R1-4)
17A	227	0.066	*h*2→*l*7; *h*3→*l*3	π(R1-3)→π*(R1-4); π(R1-4,N)→π*(R1,3,4)

Table S5. Some DFT molecular orbitals calculated for deprotonated HPPCO molecule.

MO	hartree	% contribution from each part of the compound															
		15C				6C				N				2O			
		s	p_x	p_y	p_z	s	p_x	p_y	p_z	s	p_x	p_y	p_z	s	p_x	p_y	p_z
*l*7	0.162	0	0	0	80	0	0	0	3	0	0	0	4	0	0	0	12
*l*6	0.151	0	0	0	0	0	1	19	80	0	0	0	0	0	0	0	0
*l*5	0.148	0	0	0	21	0	1	14	58	0	0	0	2	0	0	0	3
*l*4	0.134	0	0	0	94	0	0	0	0	0	0	0	0	0	0	0	5
*l*3	0.125	0	0	0	84	0	0	2	8	0	0	0	4	0	0	0	2
*l*2	0.111	0	0	0	97	0	0	0	1	0	0	0	0	0	0	0	2
*l*1	0.087	0	0	0	95	0	0	0	0	0	0	0	0	0	0	0	4
*h*1	-0.138	0	0	0	46	0	1	7	22	0	0	0	1	0	0	0	23
*h*2	-0.196	0	0	0	70	0	0	0	0	0	0	0	21	0	0	0	9
*h*3	-0.198	0	0	0	96	0	0	0	0	0	0	0	2	0	0	0	2
*h*4	-0.204	2	6	3	0	0	1	8	27	0	0	0	0	0	31	20	0
*h*5	-0.211	1	3	3	0	0	1	10	39	0	0	0	0	0	32	10	0
*h*6	-0.224	0	1	1	11	0	1	14	53	0	0	0	0	0	4	0	14
*h*7	-0.229	1	7	1	1	1	4	3	17	1	2	0	0	1	58	2	1

Table S6. ZINDO electronic states and predominant transitions of deprotonated HPPCO molecule.

State	nm	f	Predominant transition	comment
A-absorption				
1A	405	0.090	*h*1→*l*1	π(R4;O;ph)→π*(R1-4)
2A	385	0.040	*h*1→*l*1; *h*4→ *l*1	π(R4;O;ph)→π*(R1-4)
3A	341	0.262	*h*1→*l*3	π(R4;O;ph)→π*(R1-4)
4A	325	0.159	*h*2→*l*1	π(R1-4,N)→π*(R1-4)
5A	325	0.057	*h*7→*l*7,*l*1; *h*1→*l*2; *h*2→*l*1	n(O)+π(ph)→π*(R1-4); π(R4;O;ph)→π*(R1-4); π(R1-4,N)→π*(R1-4)
B-absorption				
6A	315	0.059	*h*1→*l*2,*l*5	π(R4;O;ph)→π*(R1-4),π*(ph)
7A	311	0.018	*h*1→*l*6	π(R4;O;ph)→π*(ph)
8A	307	0.263	*h*3→ *l*1	π(R1-2)→π*(R1-4)
9A	291	0.032	*h*1→*l*7,*l*4	π(R4;O;ph)→π*(R1-4;O), π*(R1-4)
10A	279	0.156	*h*3→*l*3,*l*2	π(R1-2)→π*(R1-4)
11A	275	0.007	*h*1→*l*3,*l*2, *l*5	π(R4;O;ph)→π*(R1-4),π*(ph)
12A	266	0.009	*h*1→*l*10,*l*2	π(R4;O;ph)→π*(R1-4)
C-absorption				
13A	256	0.177	*h*3→*l*3; *h*1→*l*4	π(R1-2)→π*(R1-4); π(R4;O;ph)→π*(R1-4)
14A	253	0.634	*h*2→*l*2,*l*3	π(R1-4,N)→π*(R1-4)
15A	251	0.508	*h*1→*l*7	π(R,2O,N)→π*(R)
16A	247	0.619	*h*3→*l*2, *h*2→*l*2, *h*1→*l*4	π(R1-2)→π*(R1-4)
17A	239	0.021	*h*4→ *l*1	n(O)+π(ph)→π*(R1-4)
18A	236	0.257	*h*5→*l*5; *h*6→*l*6	n(O)+π(ph)→π*(ph); π(ph)+n(O)→π*(ph)