Electronic Supplementary Material (ESI)

Supplementary Information

Table S1 The bond angle parameters of three portonated pyrene isomers. Calculated values were obtained by the CASSCF(12,10)/cc-pVDZ methods for the ground and first excited states, respectively.

	1H-P_y^+		2H-P_y^+		4H-P_y^+	
Angles (º)	S_0	S_1	S_0	S_1	S_0	S_1
C5-C1-C2	116.2	114.4	122.0	122.1	120.5	121.8
C1-C2-C3	122.4	122.6	116.8	117.1	120.9	119.3
C2-C3-C7	121.1	121.9	122.0	122.1	120.5	120.4
C5-C4-C8	120.8	121.6	120.8	120.8	116.7	114.9
C4-C8-C9	121.2	120.5	121.2	120.8	123.1	123.2
C8-C9-C10	118.6	118.7	119.3	119.6	119.1	119.8
C9-C10-C6	120.0	120.1	120.0	119.9	121.1	120.1
C9-C10-C11	119.8	119.7	119.9	120.2	118.7	119.8
C10-C11-C12	119.2	119.1	118.9	118.7	118.5	120.1

Table S2 The Cartesian coordinates (in Å) of the ground and first excited state optimized geometries of protonated pyrene isomers calculated by CASSCF(12,10)/cc-pVDZ level.

Species	S_0				S_1			
1H-P_y^+	C	1.243985	2.870638	0.000000	C	1.211599	2.925399	0.000000
	C	-0.085683	3.534585	0.000000	C	-0.144857	3.536586	0.000000
	C	-1.244886	2.835476	0.000000	C	-1.315575	2.770944	0.000000
	C	-2.458836	0.665320	0.000000	C	-2.489976	0.595813	0.000000
	C	-1.244865	1.392449	0.000000	C	-1.283479	1.364562	0.000000
	C	0.000000	0.674129	0.000000	C	0.000000	0.683967	0.000000
	C	1.234130	1.373500	0.000000	C	1.215461	1.412788	0.000000
	C	2.443478	0.649273	0.000000	C	2.424932	0.710745	0.000000
	C	2.440793	-0.734684	0.000000	C	2.460756	-0.688457	0.000000

C	1.222248	-1.468080	0.000000	C	1.263309	-1.435244	0.000000
C	-0.006906	-0.749272	0.000000	C	0.018507	-0.736073	0.000000
C	-1.242851	-1.460581	0.000000	C	-1.217012	-1.476452	0.000000
C	-2.458746	-0.716412	0.000000	C	-2.460846	-0.781888	0.000000
C	1.191887	-2.884480	0.000000	C	1.254228	-2.862897	0.000000
C	-0.018087	-3.575527	0.000000	C	0.039519	-3.579482	0.000000
C	-1.225991	-2.871921	0.000000	C	-1.170541	-2.911521	0.000000
H	1.831082	3.234150	0.867659	H	1.780449	3.314553	0.870142
H	1.831082	3.234150	-0.867659	H	1.780449	3.314553	-0.870142
H	-0.100608	4.626813	0.000000	H	-0.218962	4.626555	0.000000
H	-2.206105	3.352413	0.000000	H	-2.282908	3.279857	0.000000
H	-3.403416	1.211384	0.000000	H	-3.446210	1.123885	0.000000

	H	-3.407553	-1.258028	0.000000	H	-3.389592	-1.354033	0.000000
	H	-2.173143	-3.415912	0.000000	H	-2.110748	-3.465571	0.000000
	H	-0.023469	-4.666073	0.000000	H	0.060315	-4.670608	0.000000
	H	2.134844	-3.435736	0.000000	H	2.204727	-3.400082	0.000000
	H	3.387403	-1.279656	0.000000	H	3.420484	-1.208170	0.000000
	H	3.391867	1.190022	0.000000	H	3.365847	1.266323	0.000000
2H-P_y^+	C	0.000000	0.000000	3.533510	C	0.000000	0.000000	3.603349
	C	0.000000	1.214823	2.849471	C	0.000000	1.195972	2.899825
	C	0.000000	1.243522	1.453908	C	0.000000	1.221028	1.473149
	C	0.000000	0.000000	0.734469	C	0.000000	0.000000	0.758503
	C	0.000000	-1.243522	1.453908	C	0.000000	-1.221028	1.473149
	C	0.000000	-1.214823	2.849471	C	0.000000	-1.195972	2.899825

C	0.000000	2.480089	0.720347	C	0.000000	2.426835	0.749815
C	0.000000	0.000000	-0.669824	C	0.000000	0.000000	-0.660562
C	0.000000	1.261108	-1.384862	C	0.000000	1.228900	-1.372964
C	0.000000	2.493815	-0.632820	C	0.000000	2.427503	-0.647007
C	0.000000	1.251804	-2.754946	C	0.000000	1.246277	-2.819756
H	0.000000	2.186532	-3.305385	H	0.000000	2.210430	-3.315418
C	0.000000	0.000000	-3.526143	C	0.000000	0.000000	-3.674143
C	0.000000	-1.261108	-1.384862	C	0.000000	-1.228900	-1.372964
C	0.000000	-2.493815	-0.632820	C	0.000000	-2.427503	-0.647007
C	0.000000	-2.480089	0.720347	C	0.000000	-2.426835	0.749815
H	0.000000	-3.408927	1.278790	H	0.000000	-3.370970	1.283415
H	0.000000	-3.428771	-1.180265	H	0.000000	-3.372550	-1.177325

	H	0.000000	3.408927	1.278790	H	0.000000	3.370970	1.283415
	H	0.000000	0.000000	4.617129	H	0.000000	0.000000	4.685261
	H	0.000000	2.146773	3.402124	H	0.000000	2.138616	3.437057
	H	0.000000	-2.146773	3.402124	H	0.000000	-2.138616	3.437057
	H	0.000000	3.428771	-1.180265	H	0.000000	3.372550	-1.177325
	H	-0.855463	0.000000	-4.226450	H	-0.868564	0.000000	-4.350175
	C	0.000000	-1.251804	-2.754946	C	0.000000	-1.246277	-2.819756
	H	0.000000	-2.186532	-3.305385	H	0.000000	-2.210430	-3.315418
	H	0.855463	0.000000	-4.226450	H	0.868564	0.000000	-4.350175
4H-P_y^+	C	-0.114116	3.551687	0.000000	C	0.074332	3.575830	0.000000
	C	1.117048	2.862969	0.000000	C	1.266615	2.874657	0.000000
	C	1.207142	1.458716	0.000000	C	1.249527	1.428636	0.000000

C	0.000000	0.698684	0.000000	C	0.005748	0.726486	0.000000
C	-1.271850	1.406962	0.000000	C	-1.229213	1.460300	0.000000
C	-1.294851	2.840783	0.000000	C	-1.151761	2.897838	0.000000
C	2.473263	0.776758	0.000000	C	2.443257	0.687743	0.000000
C	0.050123	-0.722438	0.000000	C	-0.009927	-0.719616	0.000000
C	1.325224	-1.379163	0.000000	C	1.223657	-1.440617	0.000000
C	2.523899	-0.585970	0.000000	C	2.434629	-0.717637	0.000000
C	1.360389	-2.787013	0.000000	C	1.213075	-2.864354	0.000000
H	2.325481	-3.297148	0.000000	H	2.163042	-3.403298	0.000000
C	0.181298	-3.522519	0.000000	C	0.004909	-3.561312	0.000000
C	-1.151208	-1.495264	0.000000	C	-1.219757	-1.428553	0.000000
C	-2.476950	-0.789899	0.000000	C	-2.538062	-0.707434	0.000000

C	-2.443043	0.681629	0.000000	C	-2.440454	0.776789	0.000000
H	-3.401428	1.210364	0.000000	H	-3.373346	1.343224	0.000000
H	-3.098191	-1.108562	0.864145	H	-3.140110	-1.049391	0.868629
H	3.389483	1.369871	0.000000	H	3.400286	1.213500	0.000000
H	-0.122338	4.642279	0.000000	H	0.082267	4.666935	0.000000
H	2.044471	3.442090	0.000000	H	2.226857	3.391716	0.000000
H	-2.258885	3.353596	0.000000	H	-2.084801	3.465240	0.000000
H	3.486410	-1.101256	0.000000	H	3.383419	-1.259144	0.000000
H	0.223201	-4.613236	0.000000	H	-0.002608	-4.651827	0.000000
C	-1.070764	-2.880707	0.000000	C	-1.192235	-2.850999	0.000000
H	-1.983630	-3.480725	0.000000	H	-2.140852	-3.393267	0.000000
H	-3.098191	-1.108562	-0.864145	H	-3.140110	-1.049392	-0.868628

Table S3 Vibrational frequencies (cm^{-1}) and Huang-Rhys factors of the lowest excited state of 1H-Py^+ calculated at B3LYP/cc-pVDZ level of theory.

1H-Py^+	Mode	[a]Exp	[b]S_0	S_1	Huang-Rhys factors (S)
No			S_0 ($^1A'$)	S_1 ($^1A'$)	
1			96	90	0
2			113	97	0
3			191	177	0
4			197	206	0
5			250	238	0
6			324	313	0
7	v_{50}	327	340	346	0.0129
8	v_{49}	394	396	389	0.0010
9			402	394	0
10	v_{48}	442	443	446	0.0695
11			473	475	0
12	v_{47}	476	481	487	0.0164
13			487	490	0.0370

14			500	494	0
15			520	521	0.0407
16			544	525	0
17	v_{44}	579	580	586	0.0459
18			642	666	0
19	v_{43}	666	666	673	0
20			670	676	0
21	v_{42}	710	710	722	0.0452
22			747	726	0
23			773	763	0
24	v_{41}	781	778	789	0.0043
25	v_{40}	808	804	813	0.0087
26			809	827	0
27	$2v_{48}$	888	867	846	0
28			874	887	0
29			896	905	0
30	v_{39}	925	926	907	0.0001
31			944	917	0
32		965	957	963	0.0001

33			980	965	0
34			981	991	0.0049
35			988	992	0
36			993	999	0
37	v_{36}	1055	1001	1009	0
38			1071	1086	0.0021
39		1126	1107	1130	0.0177
40			1124	1143	0.0063
41			1141	1153	0.0080
42			1147	1172	0
43	v_{32}	1165	1156	1184	0.0610
44			1170	1191	0.0180
45			1184	1214	0.0992
46	v_{29}	1230	1211	1230	0.1131
47		1248	1220	1238	0.0566
48	v_{27}	1258	1230	1258	0.0228
49		1306	1303	1321	0.0043
50			1317	1345	0.0005
51	v_{23}	1372	1343	1379	0.0107

52			1364	1390	0
53			1380	1403	0.0061
54	v_{21}	1404	1394	1420	0.0152
55		1412	1406	1428	0.0054
56			1411	1445	0.0010
57		1466	1436	1456	0
58	v_{17}	1480	1473	1471	0.0561
59	v_{16}	1494	1491	1488	0.0110
60	v_{15}	1519	1530	1510	0.1701
61	v_{14}	1579	1561	1527	0.0014
62	v_{13}	1606	1575	1565	0.0015
63	v_{12}	1619	1602	1592	0.0003
64		1644	1625	1620	0.0718
65		1820	2904	2963	0.0001
66		1957	2922	2974	0
67		2222	3095	3186	0.0045
68		2335	3096	3187	0.0196
69		2834	3098	3194	0.0016
70			3099	3197	0.0017

71	3047	3103	3202	0.0201
72		3109	3203	0.0013
73		3113	3206	0.0010
74		3115	3212	0.0053
75		3124	3217	0.0006

[a] From Ref. **14**. [b] NIST, (B3LYP/cc-pVDZ, 0.97)

Table S4 Vibrational frequencies (cm^{-1}) and Huang-Rhys factors of the lowest excited state of 2H-P_y^+ calculated at B3LYP/cc-pVDZ level of theory.

No	2H-P_y^+ (v*0.97)		Huang-Rhys factors (S)
	S_0 ($^1A_1$)	S_1 ($^1A'$)	S
1	83	88	0
2	140	113	0
3	202	127	0
4	215	185	0
5	229	216	0
6	288	288	0
7	345	298	0
8	370	382	0
9	394	455	1.9346
10	437	456	0
11	481	463	0.0047
12	488	485	0
13	489	490	0
14	501	506	0

15	514	511	0
16	529	529	0
17	567	536	0.0286
18	656	596	0
19	664	645	0.2945
20	674	677	0
21	717	690	0
22	734	696	0
23	770	697	0
24	771	779	0.1378
25	791	798	0
26	792	830	0.0012
27	839	866	0
28	848	871	0
29	873	899	0
30	921	911	0
31	938	954	0
32	940	964	0.2292
33	941	980	0

34	983	996	0
35	983	1008	0
36	986	1014	0.0069
37	1001	1024	0
38	1040	1024	0
39	1070	1116	0.0047
40	1092	1134	0
41	1106	1155	0
42	1129	1168	0.0650
43	1149	1182	0
44	1163	1212	0
45	1197	1215	0
46	1219	1241	0.0467
47	1221	1257	0
48	1237	1282	0.1541
49	1248	1292	0.1045
50	1327	1354	0.0113
51	1327	1365	0
52	1353	1402	0

53	1380	1403	0
54	1385	1442	0
55	1418	1451	0
56	1421	1462	0.0019
57	1428	1478	0.0028
58	1463	1491	0
59	1504	1506	0
60	1552	1548	0.0380
61	1556	1558	0
62	1598	1589	0.1545
63	1600	1642	0
64	1616	1666	0.2463
65	2881	2952	0.1299
66	2887	2966	0
67	3096	3180	0
68	3096	3182	0.0169
69	3098	3183	0.0001
70	3098	3183	0
71	3099	3186	0.0086

72	3106	3187	0
73	3113	3196	0.0893
74	3113	3197	0
75	3117	3214	0.0259

NIST, (B3LYP/cc-pVDZ, 0.97)

Table S5 Vibrational frequencies (cm^{-1}) and Huang-Rhys factors of the lowest excited state of 4H-P_y^+ calculated at B3LYP/cc-pVDZ level of theory.

No	4H-P_y^+ (ν*0.97)		Huang-Rhys factors (S)
	S_0 (^{1}A')	S_1 (^{1}A')	S
1	81	85	0
2	128	124	0
3	185	199	0
4	211	208	0
5	245	235	0
6	274	299	0
7	342	345	0.0448
8	390	390	0.1411
9	421	419	0
10	440	442	0.0449
11	466	466	0
12	482	488	0.1561
13	490	501	0.0382
14	508	517	0

15	528	527	0
16	529	552	0.3912
17	567	589	0.0033
18	607	593	0
19	668	671	0.0007
20	709	706	0.0047
21	714	722	0
22	727	733	0
23	774	771	0.0077
24	779	788	0
25	785	809	0
26	792	812	0
27	846	853	0
28	862	878	0
29	914	893	0
30	924	934	0.0124
31	942	958	0
32	962	968	0
33	977	983	0.0013

34	980	1000	0
35	994	1010	0
36	1002	1024	0
37	1029	1054	0.0053
38	1058	1089	0.0003
39	1077	1116	0.0170
40	1084	1121	0.0317
41	1137	1147	0.0580
42	1139	1169	0
43	1156	1186	0.0727
44	1163	1187	0.0086
45	1187	1202	0.0467
46	1213	1223	0.3561
47	1219	1229	0.2067
48	1232	1248	0.0507
49	1287	1318	0
50	1315	1339	0.0119
51	1320	1368	0.0663
52	1359	1379	0.0166

53	1375	1391	0.0209
54	1397	1414	0.1603
55	1406	1426	0.0127
56	1415	1448	0.0077
57	1425	1465	0.0011
58	1466	1479	0.2634
59	1503	1497	0.2543
60	1537	1530	0.0900
61	1556	1550	0.0372
62	1586	1572	0.0222
63	1594	1581	0.0002
64	1621	1634	0.0796
65	2891	2954	0.0013
66	2900	2962	0
67	3083	3192	0.0205
68	3091	3194	0.0206
69	3092	3194	0.1394
70	3097	3200	0.0275
71	3101	3201	0.1090

72	3104	3205	0.1815
73	3112	3208	0.0575
74	3117	3219	0.0009
75	3124	3222	0.0006

NIST, (B3LYP/cc-pVDZ, 0.97)