Fig. S1

Supplementary Material for PCCP

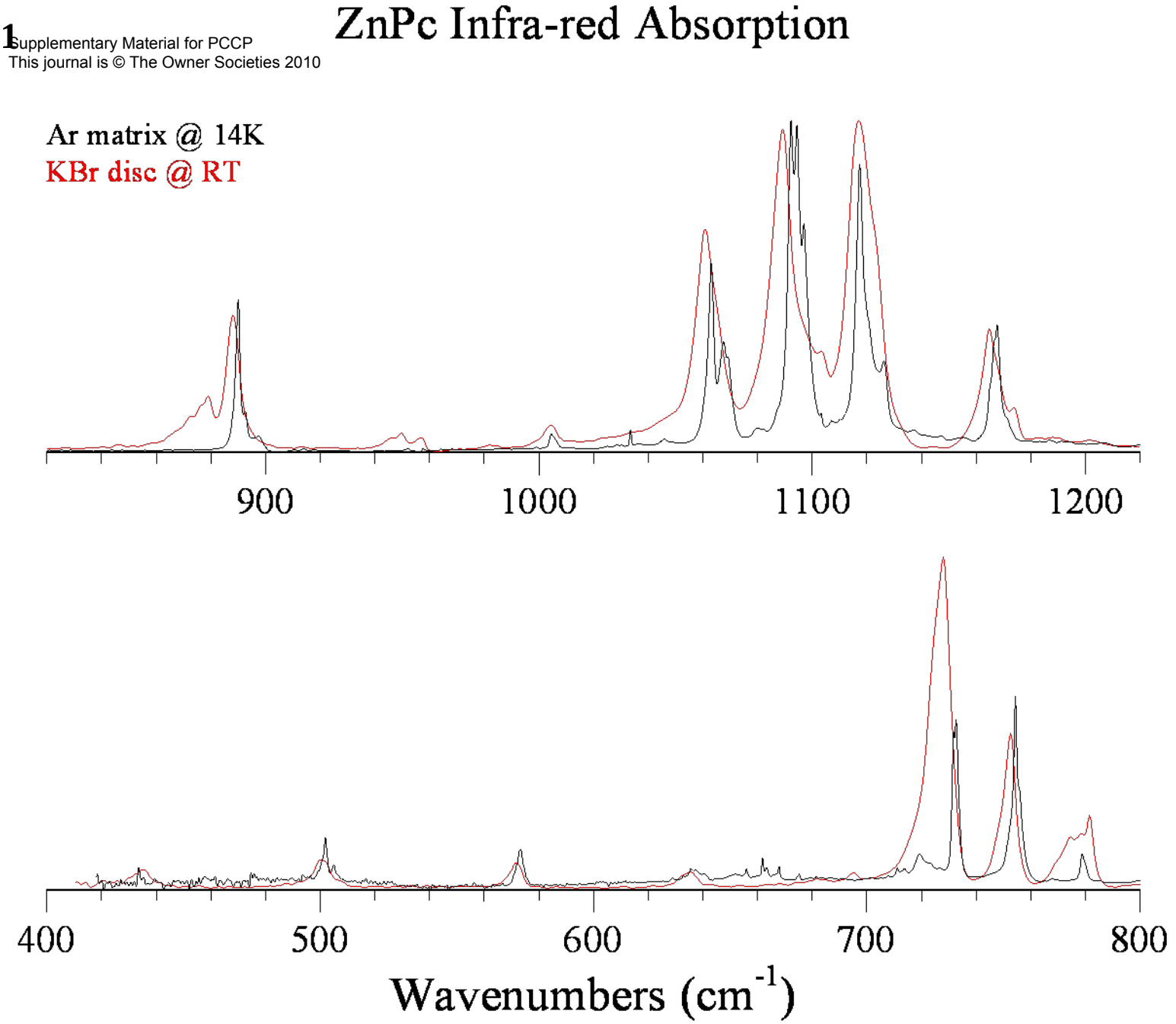


Fig. S2

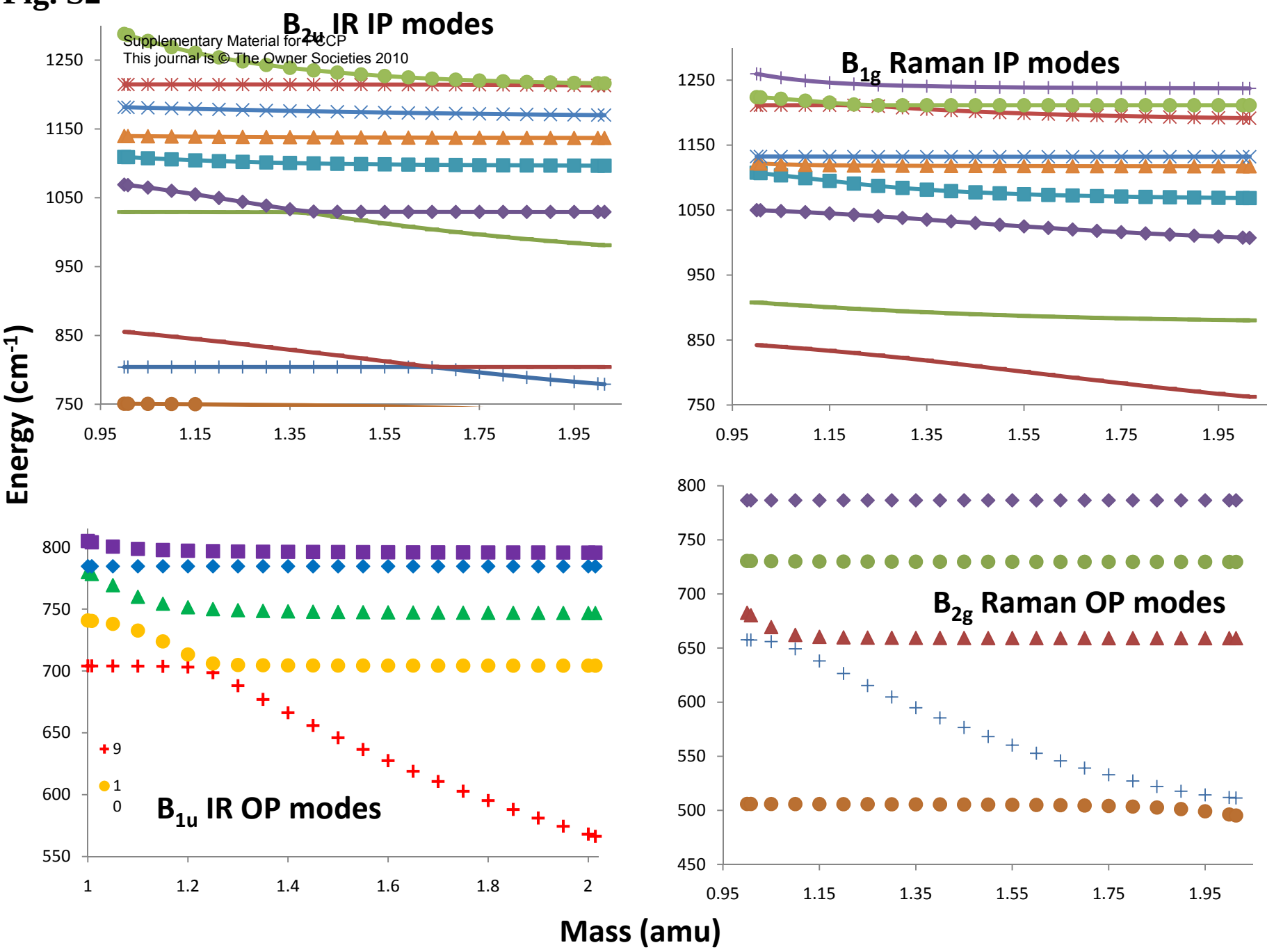
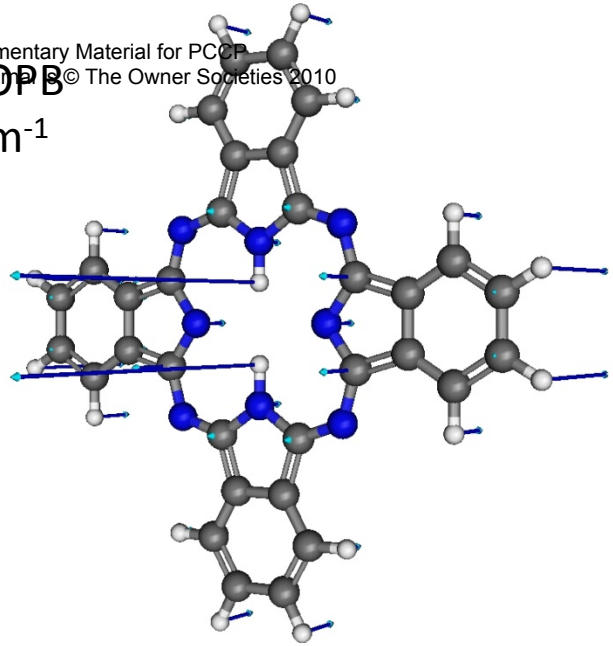
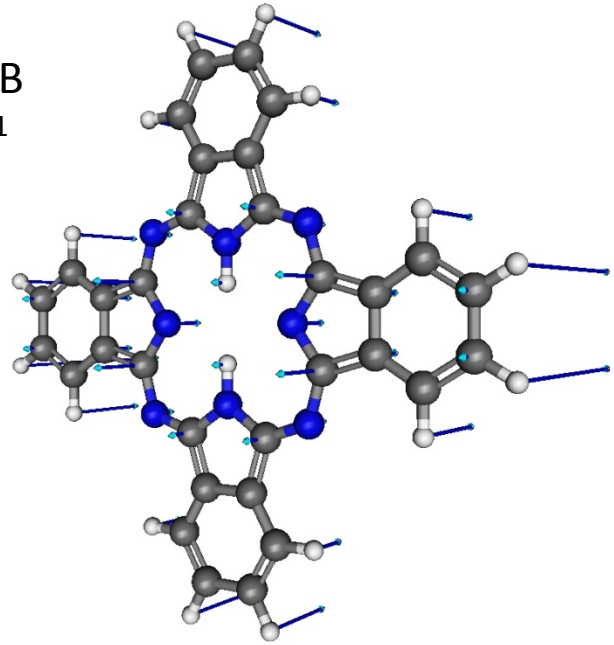


Fig. S3

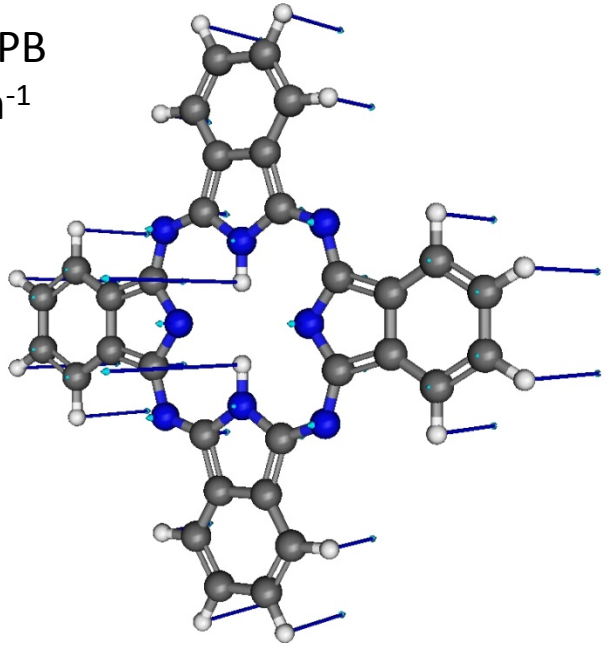
H_2Pc OPB
804 cm^{-1}



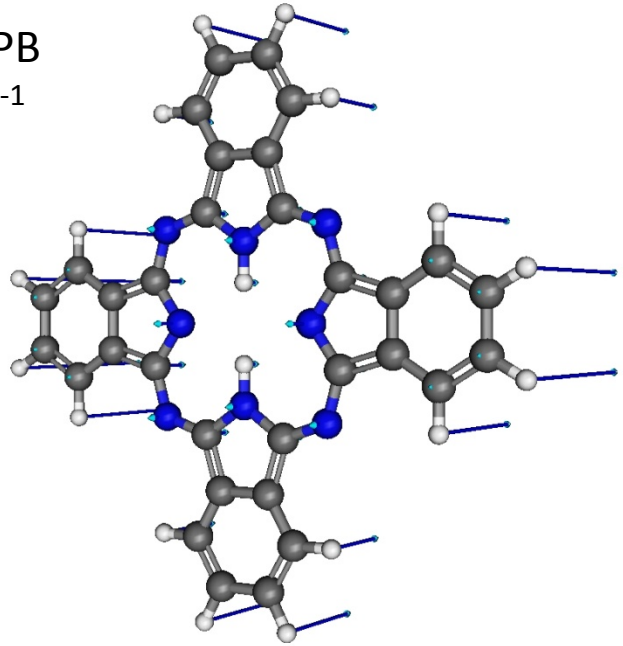
D_2Pc OPB
796 cm^{-1}



H_2Pc OPB
740 cm^{-1}



D_2Pc OPB
747 cm^{-1}



Supplementary Figure Captions

Fig. S1 A comparison of the Infrared absorption spectra recorded for ZnPc isolated in an Ar matrix at 14 K and in a KBr pellet at room temperature. Other than having larger bandwidths and consistent red-shifting, the most pronounced difference in the KBr spectrum is the increased intensity of the 727 cm^{-1} band relative to its matrix equivalent at 732.7 cm^{-1} in Ar (739.9 cm^{-1} in N_2). As found in H_2Pc, the observed difference in the two host media is an indication of the presence of ZnPc aggregates in KBr samples.

Fig. S2 DFT predictions of the isotope dependence for both the IR and Raman-active out-of-plane bending (OPB) and in-plane bending (IPB) modes of H_2Pc and D_2Pc. The mode correlations were generated by conducting frequency calculations in the mass range 1 to 2 amu in 0.05 amu increments. As indicated, the OPB exhibits a simpler behaviour where a single, nearly "pure" N-H mode can be identified, while several of the IP bending modes involve N-H motion.

Fig. S3 Vector displacement representations of the four highest energy out-of-plane N-H normal modes shown in Fig. 12 for H_2Pc and D_2Pc. The frequencies provided are unscaled DFT values.

Table S1: Bond lengths and angles determined for H_2Pc and ZnPc from DFT calculations. The atom labelling system used is provided in Fig. 1

		H_2Pc		ZnPc
Lengths	**Exp[1]**	**B3LYP**	**Exp[2]**	**B3LYP**
N-H(Zn)	0.923	1.009	1.980	1.998
N-C_α	1.377	1.375	1.369	1.369
C_α-N_m	1.326	1.313	1.331	1.327
C_α- C_β	1.453	1.450	1.455	1.459
C_β- C_β	1.398	1.409	1.400	1.407
C_β- C_γ	1.388	1.394	1.393	1.391
C_γ- C_δ	1.380	1.386	1.391	1.390
C_δ- C_δ	1.398	1.406	1.396	1.403
C_γ- H_1	0.950	1.080	NA	1.080
C_δ- H_2	0.950	1.081	NA	1.081
N'-$C_{\alpha'}$	1.369	1.362		
$C_{\alpha'}$- N_m	1.327	1.332		
$C_{\alpha'}$- $C_{\beta'}$	1.460	1.465		
$C_{\beta'}$- $C_{\beta'}$	1.395	1.400		
$C_{\beta'}$- $C_{\gamma'}$	1.391	1.389		
$C_{\gamma'}$- $C_{\delta'}$	1.387	1.392		
$C_{\delta'}$- $C_{\delta'}$	1.393	1.401		
$C_{\gamma'}$- $H_{1'}$	0.950	1.081		
$C_{\delta'}$- $H_{2'}$	0.951	1.081		
Angles				
H(Zn)-N_α-C_α	128.5	123.736	125.4	125.057
N-C_α- N_m	129.1	128.100	127.8	127.456
C_α-N-C_α	109.8	112.527	109.1	109.887
N-C_α-C_β	108.1	106.135	108.8	108.452
C_α-C_β-C_β	107.4	107.601	106.6	106.605
C_β-C_β-C_γ	120.7	120.960	121.3	121.021
C_β-C_γ-C_δ	117.7	117.829	117.3	117.836
C_γ-C_δ-C_δ	121.6	121.211	121.5	121.144
C_β-C_γ-H_1	121.2	120.586	NA	120.709
C_γ-C_δ-H_2	119.2	119.622	NA	119.638
N'-$C_{\alpha'}$- N_m	128.4	121.688		
$C_{\alpha'}$-N'-$C_{\alpha'}$	108.0	107.226		
N'-$C_{\alpha'}$-$C_{\beta'}$	109.5	110.697		
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	106.8	105.690		
$C_{\beta'}$-$C_{\beta'}$-$C_{\gamma'}$	121.8	121.223		
$C_{\beta'}$-$C_{\gamma'}$-$C_{\delta'}$	117.0	117.670		
$C_{\gamma'}$-$C_{\delta'}$-$C_{\delta'}$	121.3	121.107		
$C_{\beta'}$-$C_{\gamma'}$-$H_{1'}$	121.5	120.925		
$C_{\gamma'}$-$C_{\delta'}$-$H_{2'}$	119.3	119.636		

1. **Matsumoto, S.; Matsuhama, K.; Mizuguchi, J.,** ***Acta Crystallographica Section C*****, 1999, 55, (1), 131-133.**
2. **Scheidt, W. R.; Dow, W.,** ***Journal of the American Chemical Society*****, 2002, 99, (4), 1101-1104.**

Table S2. DFT B3LYP / 6-311++G(2d,2p) computed Infra-red frequencies (ν, cm^{-1}) and intensities (km/mole) for H_2Pc, D_2Pc and ZnPc. The symmetry labels listed for D_2Pc are also valid for H_2Pc. Both have the z-axis perpendicular to the molecular plane as explained in Ref. 28.

	H_2Pc		**D_2Pc**			**ZnPc**			**ν_H / ν_D**
	ν_H	Int	ν_D	Int	Sym	ν_{Zn}	Int	Sym	**Ratio**
1	122.96	4.73	122.90	4.73	B3u	120.61	3.60	Eu	1.0005
2	283.07	8.16	282.74	8.09	B3u	306.37	2.51	Eu	1.0012
3	502.57	6.18	502.48	6.30	B3u	511.37	7.87	Eu	1.0002
4	567.38	2.59	564.42	1.59	B3u	585.85	10.37	Eu	1.0052
5	632.31	38.21	630.00	41.13	B3u	652.85	7.78	Eu	1.0037
6	746.46	74.09	743.13	70.60	B3u	768.00	61.07	Eu	1.0045
7	799.06	9.49	796.68	11.85	B3u	814.13	0.81	Eu	1.0030
8	891.84	69.19	889.97	67.59	B3u	906.01	55.53	Eu	1.0021
9	1028.73	1.99	1028.57	1.17	B3u	1030.03	11.40	Eu	1.0002
10	1037.22	661.50	1037.12	660.35	B3u	1111.13	174.45	Eu	1.0001
11	1086.86	0.64	1085.32	0.94	B3u	1084.48	153.67	Eu	1.0014
12	1131.89	75.42	1130.74	71.07	B3u	1138.25	146.17	Eu	1.0010
13	1186.12	13.25	1185.99	14.29	B3u	1190.02	30.39	Eu	1.0001
14	1209.22	0.53	1205.74	1.17	B3u	1210.25	2.10	Eu	1.0029
15	1312.67	52.22	1312.06	50.11	B3u	1320.40	49.72	Eu	1.0005
16	1338.84	11.65	1330.91	0.00	B3u	1343.80	21.81	Eu	1.0060
17	1358.84	176.97	1355.29	186.12	B3u	1359.59	233.93	Eu	1.0026
18	1429.46	22.07	1427.69	16.16	B3u	1436.61	56.00	Eu	1.0012
19	1490.66	61.09	1490.66	60.72	B3u	1491.01	32.70	Eu	1.0000
20	1504.98	0.51	1504.97	0.43	B3u	1509.13	0.14	Eu	1.0000
21	1531.54	119.23	1531.48	121.27	B3u	1511.62	97.41	Eu	1.0000
22	1610.84	4.40	1610.83	4.49	B3u	1615.53	8.41	Eu	1.0000
23	1639.07	10.05	1639.07	10.13	B3u	1641.29	10.73	Eu	1.0000
24	3172.80	5.45	3172.80	5.45	B3u	3173.97	5.98	Eu	1.0000
25	3190.06	27.20	3190.06	27.29	B3u	3187.58	30.09	Eu	1.0000
26	3200.16	12.59	3200.16	12.63	B3u	3201.49	9.71	Eu	1.0000
27	3207.80	37.96	3207.81	37.34	B3u	3204.81	46.69	Eu	1.0000
28	3556.22	133.75	2613.61	112.94	B3u	250.27	5.38	Eu	1.3607
1	121.79	3.64	121.49	3.60	B2u	120.61	3.60	Eu	1.0025
2	275.06	0.11	272.15	0.05	B2u	306.37	2.51	Eu	1.0107
3	499.06	2.13	489.42	0.71	B2u	511.37	7.87	Eu	1.0197
4	560.32	0.01	555.40	0.59	B2u	585.85	10.37	Eu	1.0089
5	633.47	5.87	632.04	3.54	B2u	652.85	7.78	Eu	1.0023
6	750.80	67.97	735.93	84.69	B2u	768.00	61.07	Eu	1.0202
7	804.11	2.69	804.12	2.64	B2u	814.13	0.81	Eu	1.0000
8	854.68	0.25	779.19	2.07	B2u	906.01	55.53	Eu	1.0969
9	1029.32	10.98	1029.37	14.31	B2u	1030.03	11.40	Eu	0.9999
10	1068.39	28.79	981.15	88.55	B2u	1111.13	174.45	Eu	1.0889

11	1109.04	217.46	1096.50	111.67	B2u	1084.48	153.67	Eu	1.0114
12	1139.58	133.14	1136.89	51.27	B2u	1138.25	146.17	Eu	1.0024
13	1181.40	2.22	1170.12	31.92	B2u	1190.02	30.39	Eu	1.0096
14	1214.60	29.43	1212.99	0.05	B2u	1210.25	2.10	Eu	1.0013
15	1286.42	19.32	1216.31	60.00	B2u	250.27	5.38	Eu	1.0576
16	1334.09	37.10	1332.63	99.85	B2u	1320.40	49.72	Eu	1.0011
17	1339.90	114.76	1337.88	80.48	B2u	1343.80	21.81	Eu	1.0015
18	1370.56	116.07	1370.13	115.59	B2u	1436.61	56.00	Eu	1.0003
19	1473.48	96.92	1467.63	102.11	B2u	1491.01	32.70	Eu	1.0040
20	1513.99	7.08	1513.36	10.79	B2u	1509.13	0.14	Eu	1.0004
21	1529.99	31.61	1529.04	34.70	B2u	1511.62	97.41	Eu	1.0006
22	1567.89	8.45	1545.90	1.58	B2u	1359.59	233.93	Eu	1.0142
23	1625.98	12.78	1625.82	13.77	B2u	1615.53	8.41	Eu	1.0001
24	1646.78	14.96	1646.66	14.17	B2u	1641.29	10.73	Eu	1.0001
25	3176.56	6.92	3176.56	6.92	B2u	3173.97	5.98	Eu	1.0000
26	3186.53	33.00	3186.53	33.00	B2u	3187.58	30.09	Eu	1.0000
27	3203.63	47.26	3203.62	47.28	B2u	3204.81	46.69	Eu	1.0000
28	3204.82	9.17	3204.82	9.16	B2u	3201.49	9.71	Eu	1.0000
1	19.90	0.00	19.90	0.00	B1u	22.37	0.00	B2u	1.0000
2	38.47	1.53	38.26	1.50	B1u	31.61	0.57	A2u	1.0055
3	136.17	0.38	136.10	0.40	B1u	134.30	0.00	B2u	1.0005
4	217.25	7.15	214.18	7.83	B1u	249.71	0.02	A2u	1.0143
5	256.63	1.70	255.90	1.58	B1u	249.91	0.00	B2u	1.0029
6	340.23	1.66	340.23	1.66	B1u	352.00	2.18	A2u	1.0000
7	431.00	0.26	430.99	0.22	B1u	433.57	0.00	B2u	1.0000
8	444.31	14.38	443.68	15.75	B1u	446.22	12.41	A2u	1.0014
9	704.03	4.78	704.28	4.03	B1u	715.88	0.00	B2u	0.9997
10	740.49	127.16	746.78	248.74	B1u	748.97	246.81	A2u	0.9916
11	778.36	184.33	566.31	18.00	B1u	122.63	11.08	A2u	1.3744
12	784.63	23.57	784.59	15.03	B1u	788.29	0.00	B2u	1.0000
13	804.01	4.93	795.67	23.91	B1u	797.02	31.45	A2u	1.0105
14	975.37	1.84	975.37	1.88	B1u	978.41	3.74	A2u	1.0000
15	980.94	1.97	980.93	1.82	B1u	977.91	0.00	B2u	1.0000

Table S3: DFT B3LYP / 6-311++G(2d,2p) computed Raman frequencies (cm^{-1}) and scattering activities ($Å^4$/amu) for H_2Pc, D_2Pc and ZnPc. The symmetry labels listed for D_2Pc are also valid for H_2Pc. As in the previous table, the symmetry labels used have, as explained in Ref. 28, the z-axis perpendicular to the molecular plane in all cases. The values shown in italics represent the best mode association between H_2Pc, D_2Pc and ZnPc.

	H_2Pc		**D_2Pc**			**ZnPc**			**ν_H / ν_D**
	ν_H	Int	ν_D	Int	Sym	ν_{Zn}	Int	Sym	**Ratio**
1	132.88	32.17	132.66	32.12	Ag	157.58	19.82	B1g	1.0016
2	229.72	74.90	229.34	74.54	Ag	258.37	76.58	A1g	1.0016
3	551.31	38.40	550.28	39.46	Ag	562.60	8.86	B1g	1.0019
4	577.52	49.75	575.39	47.62	Ag	600.07	116.02	A1g	1.0037
5	690.37	377.39	690.31	382.41	Ag	689.90	318.35	A1g	1.0001
6	743.52	1177.46	739.95	1131.63	Ag	764.79	928.75	B1g	1.0048
7	779.27	14.02	778.65	30.22	Ag	788.74	380.92	B1g	1.0008
8	810.69	172.30	805.98	178.69	Ag	851.61	172.77	A1g	1.0058
9	1029.03	242.78	1028.88	255.13	Ag	1029.79	244.29	B1g	1.0001
10	1029.67	562.80	1029.62	553.30	Ag	1030.45	527.33	A1g	1.0000
11	1138.32	1089.91	1135.53	1036.39	Ag	1146.80	1266.13	A1g	1.0025
12	1164.00	2523.97	1162.81	2528.87	Ag	1164.30	2844.76	B1g	1.0010
13	1185.19	352.54	1185.16	348.43	Ag	1186.33	409.97	A1g	1.0000
14	1203.96	998.66	1200.75	665.94	Ag	1202.09	1319.63	B1g	1.0027
15	1327.29	5525.98	1323.34	5987.30	Ag	1323.12	5181.51	B1g	1.0030
16	1360.92	2581.95	1355.50	2828.61	Ag	1363.78	2102.53	A1g	1.0040
17	1373.33	2815.23	1373.11	2646.15	Ag	1368.90	1713.40	B1g	1.0002
18	1422.37	479.56	1419.24	371.63	Ag	1421.41	588.56	A1g	1.0022
19	1460.91	490.84	1460.85	477.32	Ag	1455.62	478.64	A1g	1.0000
20	1481.64	1758.49	1481.63	1759.71	Ag	1478.71	2000.23	B1g	1.0000
21	1541.07	1810.91	1541.07	1815.39	Ag	1529.73	689.94	A1g	1.0000
22	1582.92	18943.34	1582.77	18899.00	Ag	1557.23	19777.07	B1g	1.0001
23	1611.42	108.35	1611.42	108.39	Ag	1614.66	85.11	B1g	1.0000
24	1626.52	39.91	1626.51	40.21	Ag	1617.53	121.12	A1g	1.0000
25	3186.54	633.00	3186.54	633.07	Ag	3187.54	674.71	B1g	1.0000
26	3190.08	678.73	3190.08	678.62	Ag	3187.64	626.18	A1g	1.0000
27	3203.69	717.09	3203.69	717.21	Ag	3204.75	97.81	B1g	1.0000
28	3207.86	785.98	3207.86	786.17	Ag	3204.99	1444.68	A1g	1.0000
29	3612.04	13.17	2649.28	35.98	Ag				1.3634
1	56.85	0.09	56.85	0.09	B3g	60.13	0.15	Eg	1.0000
2	126.40	5.39	126.40	5.39	B3g	125.24	5.12	Eg	1.0000
3	232.80	1.96	232.80	1.96	B3g	235.35	2.24	Eg	1.0000
4	287.33	0.07	287.33	0.07	B3g	288.36	0.04	Eg	1.0000
5	430.59	0.02	430.59	0.02	B3g	433.50	0.00	Eg	1.0000
6	503.88	0.01	503.88	0.01	B3g	508.73	0.03	Eg	1.0000
7	648.09	0.01	648.09	0.01	B3g	659.12	0.03	Eg	1.0000
8	740.37	0.42	740.37	0.42	B3g	739.11	0.40	Eg	1.0000

9	793.08	16.26	793.08	16.26	B3g	792.07	16.68	Eg	1.0000
10	802.06	6.87	802.06	6.87	B3g	809.00	2.40	Eg	1.0000
11	896.46	0.48	896.46	0.48	B3g	897.77	0.40	Eg	1.0000
12	975.36	0.02	975.36	0.02	B3g	978.15	0.26	Eg	1.0000
13	1008.46	0.44	1008.46	0.44	B3g	1006.68	0.21	Eg	1.0000
1	52.87	0.15	52.47	0.16	B2g	60.13	0.15	Eg	1.0075
2	116.84	4.44	116.46	4.38	B2g	125.24	5.12	Eg	1.0032
3	220.35	2.67	214.42	2.64	B2g	235.35	2.24	Eg	1.0276
4	271.88	0.02	271.83	0.03	B2g	288.36	0.04	Eg	1.0002
5	431.40	0.07	430.37	0.09	B2g	433.50	0.00	Eg	1.0024
6	505.86	0.02	511.42	0.00	B2g	508.73	0.03	Eg	0.9891
7	657.47	0.16	659.10	0.18	B2g	659.12	0.03	Eg	0.9975
8	680.33	0.04	495.23	0.03	B2g				1.3738
9	730.47	1.60	729.66	1.62	B2g	739.11	0.40	Eg	1.0011
10	786.56	15.21	786.54	15.19	B2g	792.07	16.68	Eg	1.0000
11	810.37	0.90	810.28	0.87	B2g	809.00	2.40	Eg	1.0001
12	898.03	0.30	898.03	0.30	B2g	897.77	0.40	Eg	1.0000
13	980.86	0.72	980.85	0.71	B2g	978.15	0.26	Eg	1.0000
14	1004.59	0.12	1004.59	0.12	B2g	1006.68	0.21	Eg	1.0000
1	84.78	5.07	84.24	4.93	B1g	112.54	12.92	B2g	1.0064
2	181.25	28.90	179.15	28.05	B1g	231.86	31.49	B2g	1.0117
3	211.90	1.34	211.68	1.69	B1g	213.89	0.00	A2g	1.0011
4	487.58	134.53	486.28	138.50	B1g	489.67	115.86	B2g	1.0027
5	580.49	1.99	563.31	1.81	B1g	588.59	0.00	A2g	1.0305
6	612.25	0.58	599.53	0.01	B1g	629.19	0.00	A2g	1.0212
7	699.34	3.15	696.47	2.36	B1g	701.63	4.69	B2g	1.0041
8	*841.82*	*1.14*	*880.30*	*0.00*	B1g	*864.41*	*0.00*	*A2g*	0.9563
9	*907.44*	*1.12*	*762.54*	*5.27*	B1g				1.1900
10	1049.73	227.80	1007.27	134.25	B1g	1056.58	115.99	B2g	1.0422
11	1106.98	43.02	1068.51	65.13	B1g	963.56	42.27	B2g	1.0360
12	1121.65	0.12	1117.37	29.74	B1g	1116.17	0.00	A2g	1.0038
13	1132.51	411.86	1132.15	424.96	B1g	1131.91	375.42	B2g	1.0003
14	1211.42	271.33	1211.42	260.77	B1g	1208.88	0.00	A2g	1.0000
15	1223.56	520.38	1191.40	58.66	B1g	1157.23	0.00	A2g	1.0270
16	1258.70	73.14	1237.35	535.53	B1g	1232.04	741.76	B2g	1.0173
17	1322.50	156.25	1322.34	145.67	B1g	1325.10	0.00	A2g	1.0001
18	1339.32	336.17	1339.09	353.25	B1g	1331.44	454.81	B2g	1.0002
19	1458.98	554.95	1452.44	568.44	B1g	1457.03	323.28	B2g	1.0045
20	1504.73	81.21	1504.73	82.33	B1g	1507.69	0.00	A2g	1.0000
21	1515.01	167.52	1514.97	161.82	B1g	1509.64	222.51	B2g	1.0000
22	1565.84	3.16	1549.62	13.84	B1g	1484.87	0.00	A2g	1.0105
23	1639.07	0.05	1638.96	0.12	B1g	1640.17	0.00	A2g	1.0001
24	1646.82	71.75	1646.71	71.82	B1g	1642.50	31.02	B2g	1.0001
25	3172.80	189.65	3172.80	189.66	B1g	3173.95	0.00	A2g	1.0000
26	3176.57	219.98	3176.57	219.98	B1g	3173.99	400.78	B2g	1.0000
27	3200.16	164.45	3200.16	164.45	B1g	3201.40	0.00	A2g	1.0000

28	3204.82	170.82	3204.82	170.78	B1g	3201.57	344.47	B2g	1.0000