Supporting Information

Proton-Coupled Electron Transfer of Plastoquinone Redox Reactions in Photosystem II: A Pump−Probe Ultraviolet Resonance Raman Study

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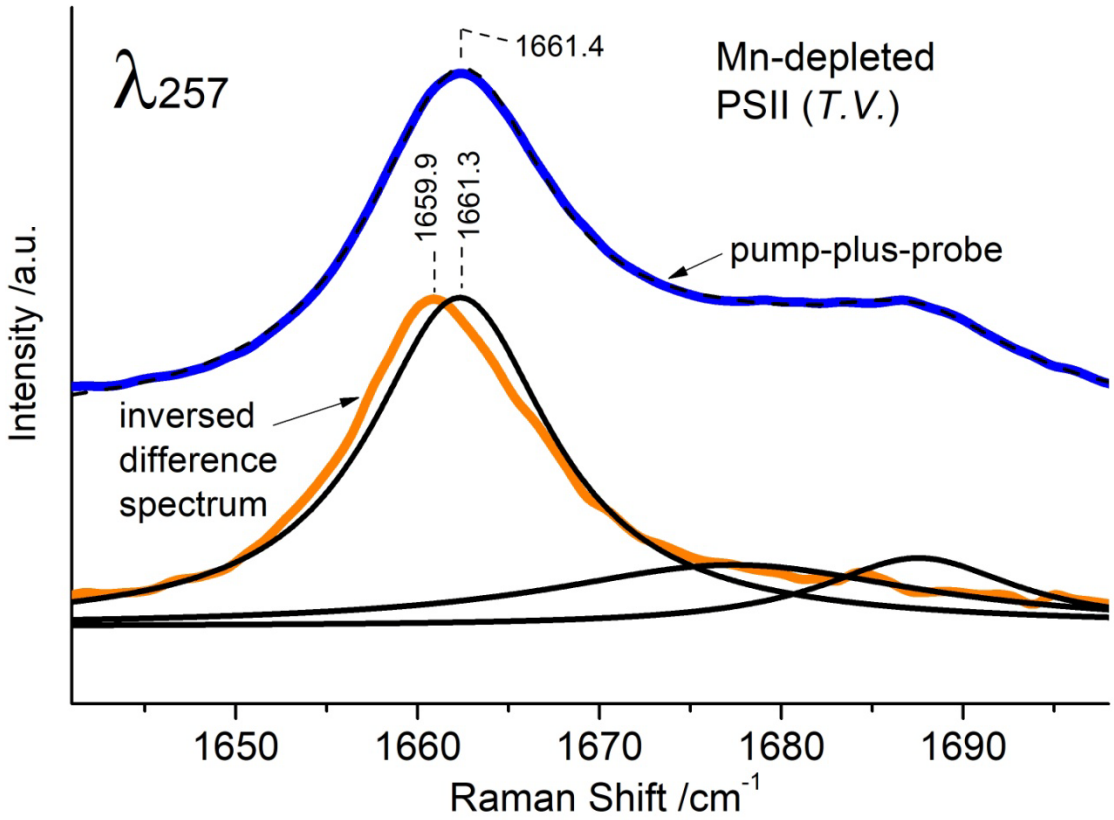

Figure S1. The precise frequencies of the PQ *ν*8a mode on the pump-plus-probe spectrum (blue, Figure 3Bb) and the inversed difference spectrum (orange, Figure 3Bc) for the Mn-depleted PSII sample. The three bands in black are the Lorentz fittings of the pump-plus-probe spectrum, and the dashed black curve is the cumulative fitting. For comparison purposes, the inversed difference spectrum and the fitting band at 1661.3 cm^{-1} are both normalized. For clarity, spectra are offset along the *y* axis.

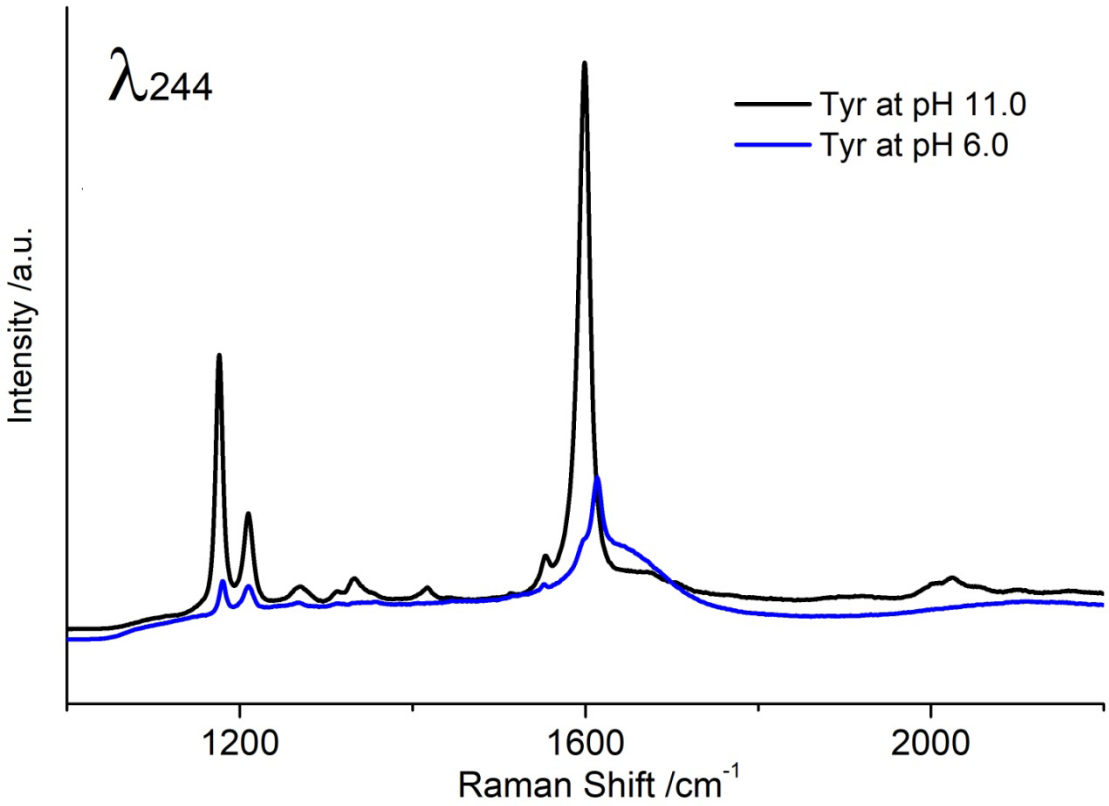

Figure S2. The 244 nm-excited Raman spectra of the tyrosine solutions at pH 6.0 and pH 11.0.

Table S1. Calculated Vibrational Frequencies and Raman Activities of the Tyrosyl Radical

description	frequency (cm^{-1})	Raman activity	description	frequency (cm^{-1})	Raman activity
N-H stretch	3529	62.1	C-H bend (ring)	984	20.8
N-H stretch	3417	831.4	C-H bend (ring)	974	109.8
C-H stretch (ring)	3136	723.7	C-C bend	943	1951.0
C-H stretch (ring)	3134	190.0	C-C bend	875	25.7
C-H stretch (ring)	3109	100.0	C-C bend	847	1194.8
C-H stretch (ring)	3107	124.4	ring breathing	836	141.3
C-H stretch	3049	60.9	ring breathing	817	630.3
C-H stretch	3009	55.9	ring/chain torsion	799	5.1
C-H stretch	2994	82.3	C-H bend (ring), N-H bend	793	229.9
C=O stretch (carboxyl)/N-H bend	1654	4498.8	C-H bend (ring), N-H bend	790	287.3
CC symmetric stretch (ring)	1586	8148.5	ring torsion, chain torsion	755	47.8
N-H bend	1569	416.3	ring torsion, chain torsion	715	170.6
CO stretch (ring)	1503	2317.0	chain bend	662	237.0
CC stretch (ring)	1481	17.6	ring bend	626	1.8
C-H bend	1467	73.5	ring bend, chain bend	548	136.1
CC stretch (ring)	1443	189.2	ring torsion, chain torsion	510	577.1
ring CC stretch/CH bend	1408	1953.2	ring stretch	481	442.2
C-H bend	1360	442.6	ring rock	458	3.3
C-C stretch (ring)	1318	340.2	ring torsion, chain torsion	397	45.7
C-C stretch/C=O stretch (carboxyl)	1296	82.8	C-C bend, C-N bend	391	22.0
N-H bend, C-H bend	1269	2874.0	C-N torsion	362	350.0
C-C stretch (ring), C-H bend	1252	79.3	C-C bend	332	180.7

C-H bend	1244	2732.2	C-N torsion	306	274.8
C-C stretch	1219	486.9	C-C bend	285	570.9
C-H bend	1192	86.8	C-C bend	175	133.0
C-H bend (ring)	1155	1974.7	C-C bend	159	4.7
C-H bend	1134	1558.2	C-C bend	87	47.6
C-H bend	1101	198.6	C-C bend	61	15.8
C-N stretch	1051	156.2	C-C torsion	47	7.5
ring distortion	990	125.0	ring bend, C-C bend	39	32.4

B3LYP density functional method and a 6-311++G(d,p) basis set were used for calculations. Modes above 1000 cm^{-1} were scaled by 0.9867.

Table S2. Calculated Vibrational Frequencies and Raman Activities of a Model PQ Anion Radical, which Has the Isoprenyl Chain Replaced by a Pentenyl Group

description	frequency (cm^{-1})	Raman activity	description	frequency (cm^{-1})	Raman activity
C-H stretch (ring)	3097	81.2	C-C stretch, C-H bend (methyl)	1090	5.8
C-H stretch (pentenyl)	3066	48.3	C-H bend (pentenyl)	1082	2.5
C-H stretch (methyl)	3058	30.8	C-H bend (methyl)	1039	0.1
C-H stretch (methyl)	3055	44.5	C-C stretch (pentenyl), C-H bend (pentenyl)	1024	7.7
C-H stretch (pentenyl)	3054	85.9	C-H bend (pentenyl)	1008	0.4
C-H stretch (pentenyl)	3037	46.7	C-H bend (pentenyl)	1003	0.8
C-H stretch (pentenyl)	2980	94.7	methyl bend (ring)	985	11.5
C-H stretch (pentenyl)	2975	161.9	C-H bend (pentenyl)	959	2.5
C-H stretch (methyl)	2972	40.5	C-H bend	956	3.4
C-H stretch (pentenyl)	2970	102.3	ring distortion, C-H bend	933	6.2
C-H stretch (methyl)	2968	272.2	C-H bend	886	1.7
C-H stretch (pentenyl)	2963	329.2	C-H bend	874	2.3
C-H stretch (pentenyl)	2943	678.2	C-C stretch (ring)	856	4.0
C-H stretch (methyl)	2939	401.2	C-C stretch (pentenyl)	782	8.6
C-H stretch (methyl)	2937	170.0	ring torsion	764	0.6
C-H stretch (pentenyl)	2935	129.5	ring torsion	710	10.6
C=C stretch (pentenyl)	1696	164.3	ring torsion	690	1.8
ring C=C/C=O symmetric stretch	1611	358.9	ring torsion	663	3.5
ring C=C antisymmetric stretch	1509	10.7	ring breathing, pentenyl torsion	605	16.0
ring CO antisymmetric stretch	1482	8.6	ring torsion, C-C bend (pentenyl)	534	0.7
C-H bend (methyl)	1481	12.3	ring stretch	506	8.1
ring C=O/C=C symmetric stretch	1473	371.9	ring stretch, pentenyl torsion	493	7.8
C-H bend (pentenyl)	1472	34.7	ring bend	482	9.3
C-H bend (methyl)	1467	9.5	C-C bend (pentenyl)	439	1.1
C-H bend (pentenyl)	1465	3.4	ring CO bend	407	1.9

C-H bend (pentenyl)	1463	9.0	C-C bend (pentenyl)	398	0.9
C-H bend (methyl)	1461	0.9	ring torsion	376	1.0
C-H bend (methyl)	1451	4.9	ring bend	334	2.0
C-H bend (pentenyl)	1449	12.9	methyl-ring bend	313	1.5
C-H bend (pentenyl)	1445	17.5	torsion	298	1.1
ring torsion	1406	8.6	torsion	283	2.1
C-H bend (pentenyl)	1391	24.0	torsion	265	1.4
C-H bend (pentenyl)	1380	8.6	pentenyl torsion	216	0.7
C-H bend (methyl)	1362	37.3	pentenyl torsion	190	0.3
C-H bend	1358	18.0	torsion	171	0.5
C-H bend	1352	11.8	pentenyl torsion	147	0.6
C-C stretch (ring), C-H bend	1314	5.7	methyl wagging	132	0.1
C-C stretch (ring), C-H bend	1254	6.7	methyl torsion	121	1.7
C-C stretch (ring), C-H bend	1215	28.2	torsion	95	0.5
C-C stretch (ring), C-H bend	1197	0.8	methyl torsion	84	2.0
C-H bend (ring)	1168	6.5	torsion	67	2.2
C-H bend	1155	12.8	torsion	32	4.0
C-C stretch, C-H bend	1114	2.0	torsion	18	2.3
C-C stretch, C-H bend	1102	23.3			

B3LYP density functional method and a 6-311++G(d,p) basis set were used for calculations. Modes above 1000 cm^{-1} were scaled by 0.9837.

Table S3. Calculated Vibrational Frequencies and Raman Activities of a Model PQH Molecule, which Has the Isoprenyl Chain Replaced by a Pentenyl Group

description	frequency (cm^{-1})	Raman activity	description	frequency (cm^{-1})	Raman activity
O-H stretch	3761	117.1	ring bend, pentenyl bend	1117	5.9
C-H stretch (ring)	3144	86.0	ring bend, pentenyl bend	1107	3.7
C-H stretch (ring)	3092	58.3	pentenyl bend	1085	1.4
C-H stretch (ring)	3083	37.4	ring torsion	1084	1.4
C-H stretch (pentenyl)	3069	28.0	C-C bend	1038	0.1
C-H stretch (pentenyl)	3067	97.5	C-C bend (pentenyl)	1027	2.7
C-H stretch (pentenyl)	3049	48.4	C-C torsion (ring)	1014	0.1
C-H stretch (ring)	3013	101.2	C-C torsion (pentenyl)	998	0.6
C-H stretch (pentenyl)	3009	89.0	C-C torsion (ring)	987	2.2
C-H stretch (pentenyl)	3002	180.4	C-C bend	962	1.5
C-H stretch (pentenyl)	2999	40.7	C-C bend	955	0.7
C-H stretch (ring)	2989	91.3	ring torsion/C-C bend	916	2.8
C-H stretch (pentenyl)	2975	194.1	C-C bend/C-H bend	890	0.2
C-H stretch (ring)	2970	314.1	C-C bend	880	2.7
C-H stretch (pentenyl)	2965	373.4	ring bend/C-C bend	843	5.5
C-H stretch (pentenyl)	2957	116.0	C-C stretch (pentenyl)	784	7.1
C-H stretch (ring)	2950	227.5	C-H bend (ring)	734	0.3
C=C stretch (pentenyl)	1702	92.4	C-C torsion (ring)	697	2.3
CC stretch (ring)	1584	91.0	ring torsion	670	3.1
C=C asymmetric stretch (pentenyl)/O-H bend	1546	11.3	ring twist	643	2.4
C-H bend (ring)	1486	4.6	ring breathe	604	15.3
C-H bend (ring)	1482	18.6	pentenyl bend	534	0.5
C=O stretch/C-H bend	1476	119.2	C-H bend (ring)/ pentenyl bend	506	1.4
C-H bend (pentenyl)	1474	50.3	ring stretch/ pentenyl bend	493	9.9
C-H bend (pentenyl)	1468	1.0	ring torsion	479	7.1
C-H bend (ring)	1467	12.5	C-O bend (ring)/C-C bend (pentenyl)	448	0.7
C-H bend (pentenyl)	1465	1.4	ring twist	396	1.5

C-H bend (ring)	1450	11.3	C-O bend (ring)/C-C bend	393	1.4
C-H bend (ring)	1449	13.4	ring bend/C-C bend	361	0.7
C-H bend (ring)	1446	6.4	C-C bend (ring)	338	0.2
C-C bend (ring)/C-H bend (ring)	1417	42.2	C-C bend	332	0.9
C-H bend (pentenyl)	1398	17.1	C-C bend (pentenyl)	302	0.4
C-H bend (ring)	1390	13.1	pentenyl bend	286	1.3
C-H bend (pentenyl)	1388	7.1	ring twist	268	1.4
C-H bend (ring)/C-C bend (ring)	1380	6.6	pentenyl twist	218	1.4
C-H bend (ring)/C-C bend (ring)	1369	5.3	pentenyl twist	188	0.5
C-H bend (pentenyl)/C-C stretch	1359	11.9	ring bend	165	0.3
C-H bend (pentenyl) /O-H bend (ring)	1317	12.8	C-C twist (ring)	149	0.8
C-C stretch (pentenyl) /O-H bend (ring)	1298	2.3	C-H bend (pentenyl)	144	0.4
C-H bend (ring)/C-H bend (pentenyl)	1249	8.2	C-H bend (ring)	128	0.5
C-H bend (ring)/ pentenyl torsion	1236	8.7	pentenyl bend	94	0.4
ring torsion	1202	5.7	C-H bend (ring)	77	0.3
pentenyl bend	1172	2.1	pentenyl bend	74	1.5
ring bend/C-H bend	1158	12.2	pentenyl bend	34	4.0

B3LYP density functional method and a 6-311++G(d,p) basis set were used for calculations. Modes above 1000 cm^{-1} were scaled by 0.9837.