Electrochemical Surface-Enhanced Raman Spectroscopy (E-SERS) of Novel Biodegradable Ionic Liquids

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SUPPORTING INFORMATION

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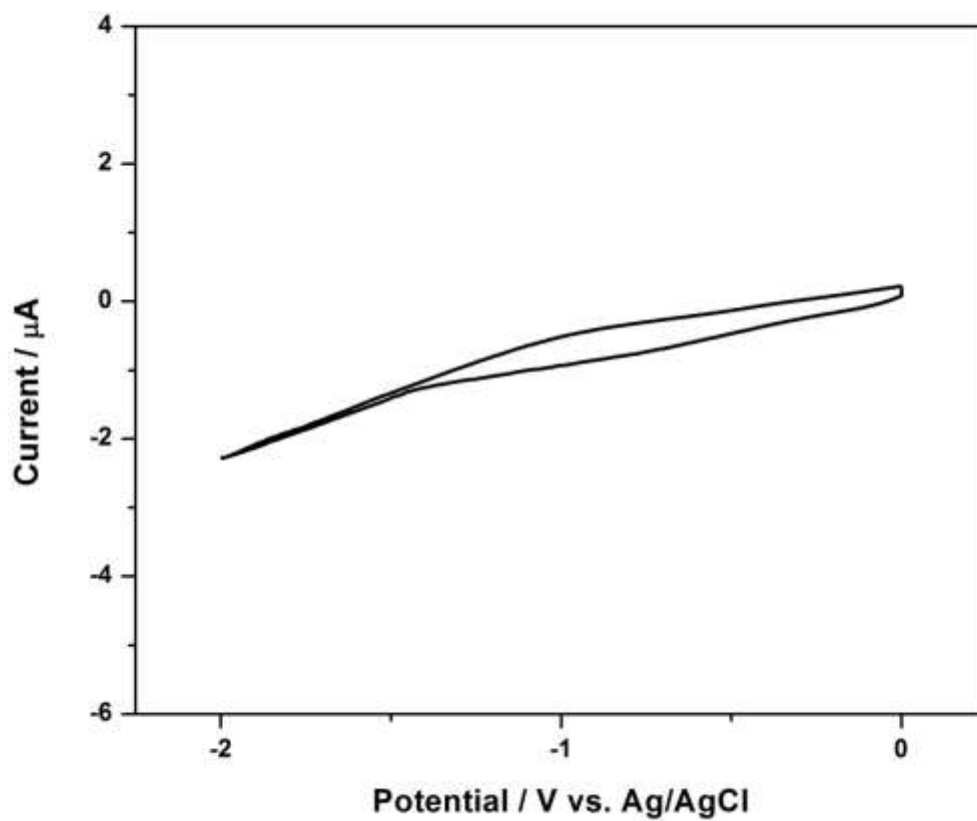Australia

Figure S1. Cyclic voltammogram of pure 3-(*sec*-butoxycarbonyl)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL recorded on a SPE. Scan rate 20 mV s^{-1}. Potential range 0.0 to -2.0 V vs Ag/AgCl.
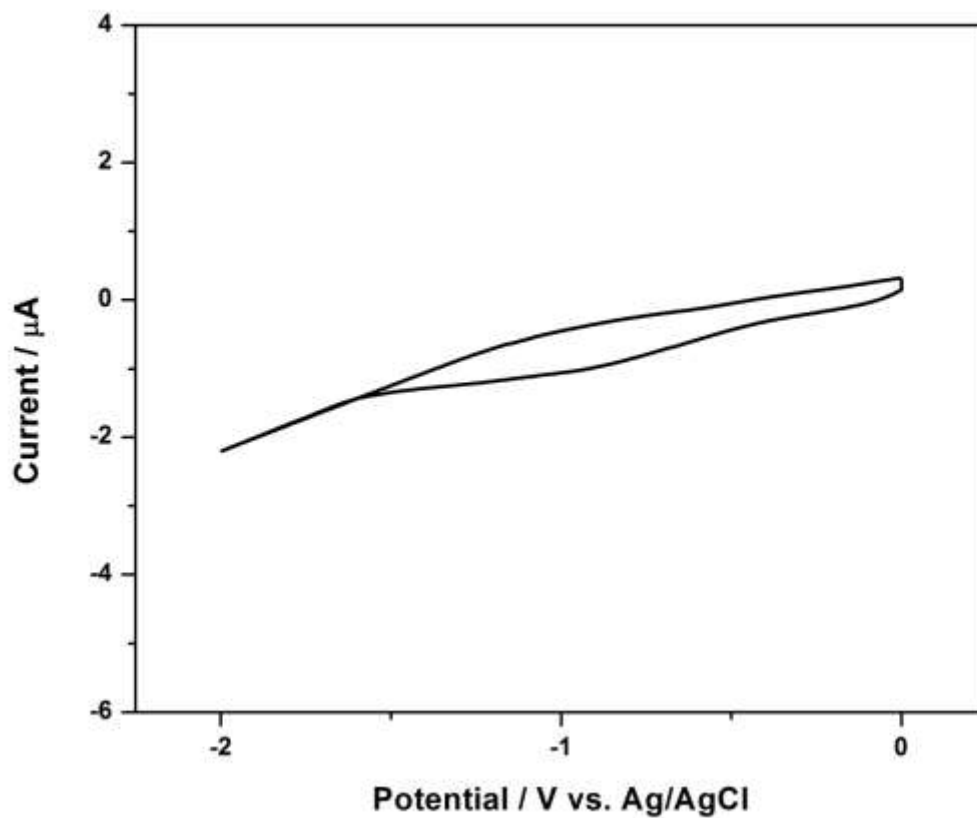
Figure S2. Cyclic voltammogram of pure 3-(*tert*-butoxycarbonyl)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL recorded on a SPE. Scan rate 20 mV s^{-1}. Potential range 0.0 to -2.0 V vs Ag/AgCl.
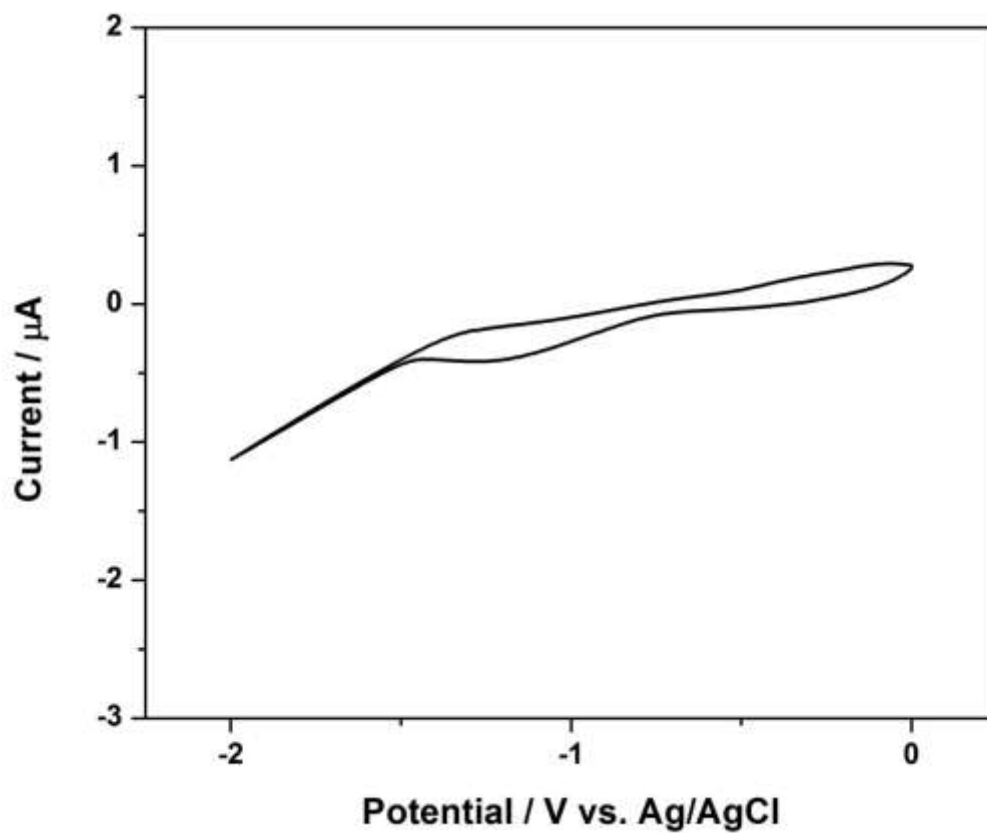
Figure S3. Cyclic voltammogram of pure 3-(n-butoxycarbonyl)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL recorded on a SPE. Scan rate 20 mV s^{-1}. Potential range 0.0 to -2.0 V vs Ag/AgCl.

Figure S4. E-SERS spectra for the 0.1 M methanolic solution of 3-(*sec*-butoxycarbonyl)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL. Collection time for each spectrum 30s, 55.9 mW.

Figure S5. E-SERS spectra for the 0.1 M methanolic solution of 3-(*n*-butoxycarbonyl)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL. Collection time for each spectrum 30s, 55.9 mW.

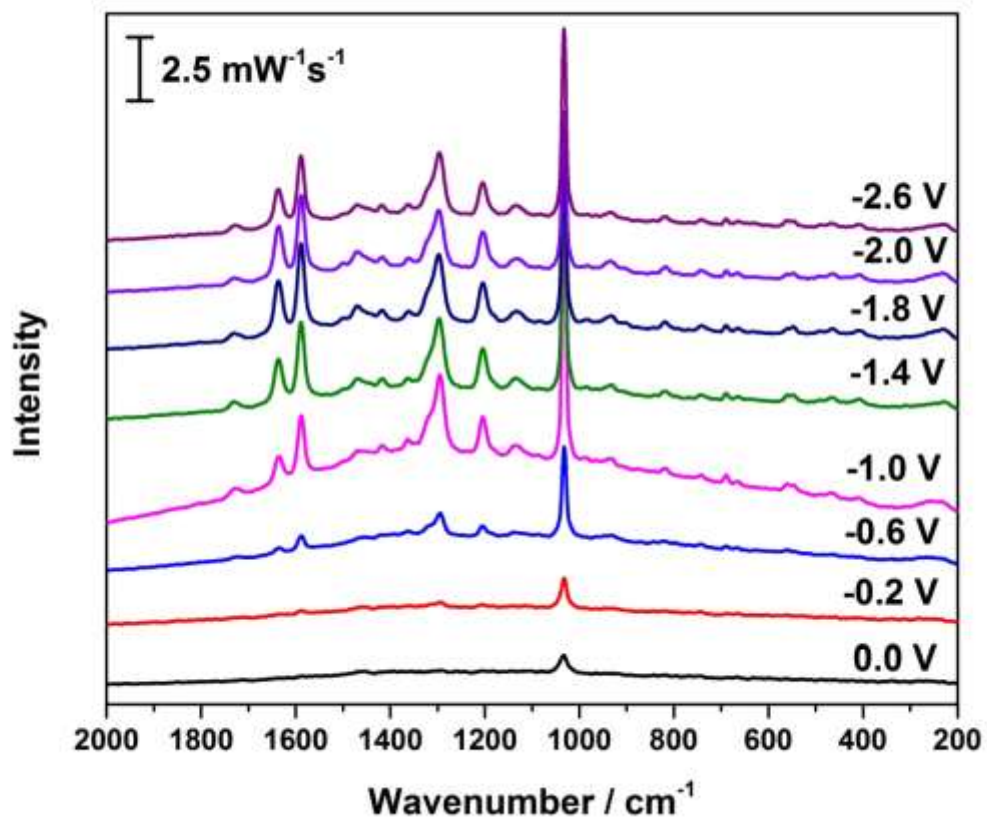Figure S6. E-SERS spectra for the 0.1 M methanolic solution of 3-(*tert*-butoxycarbonyl)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL. Collection time for each spectrum 30s, 55.9 mW.
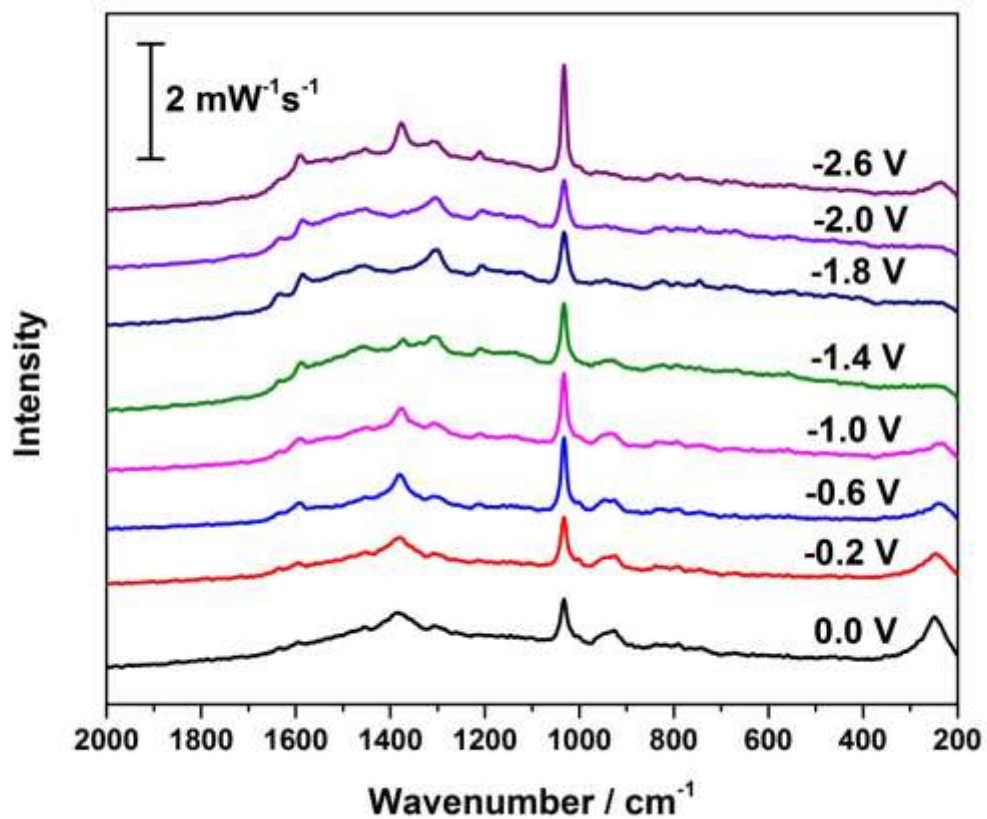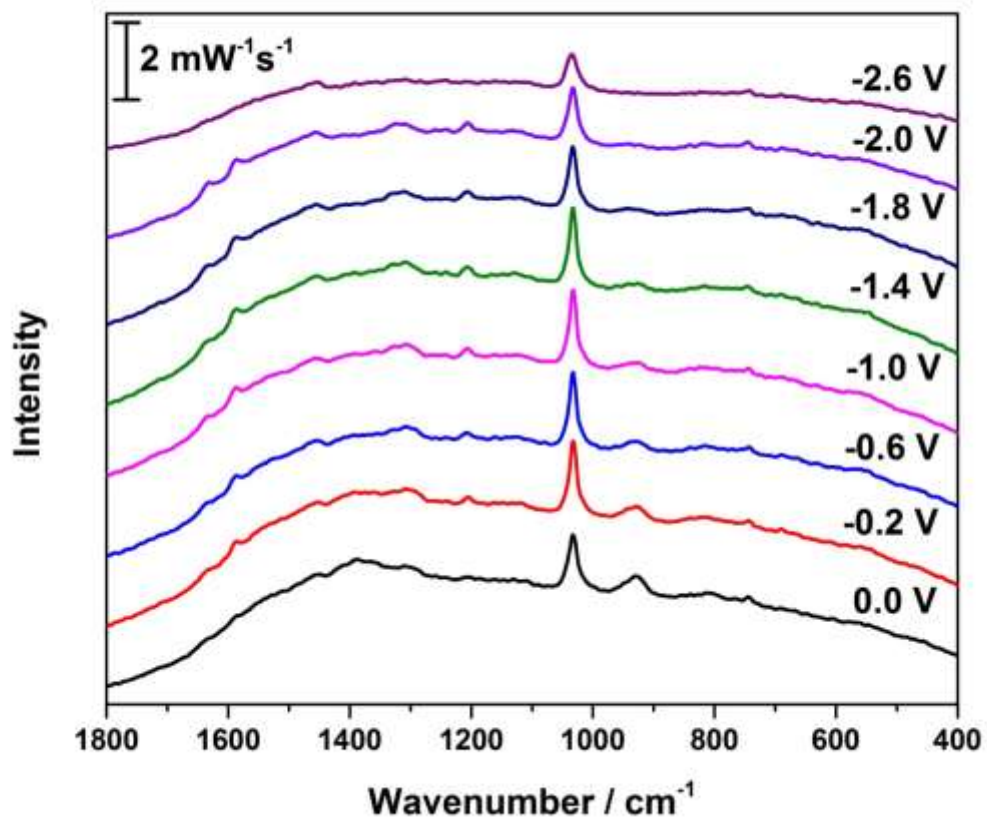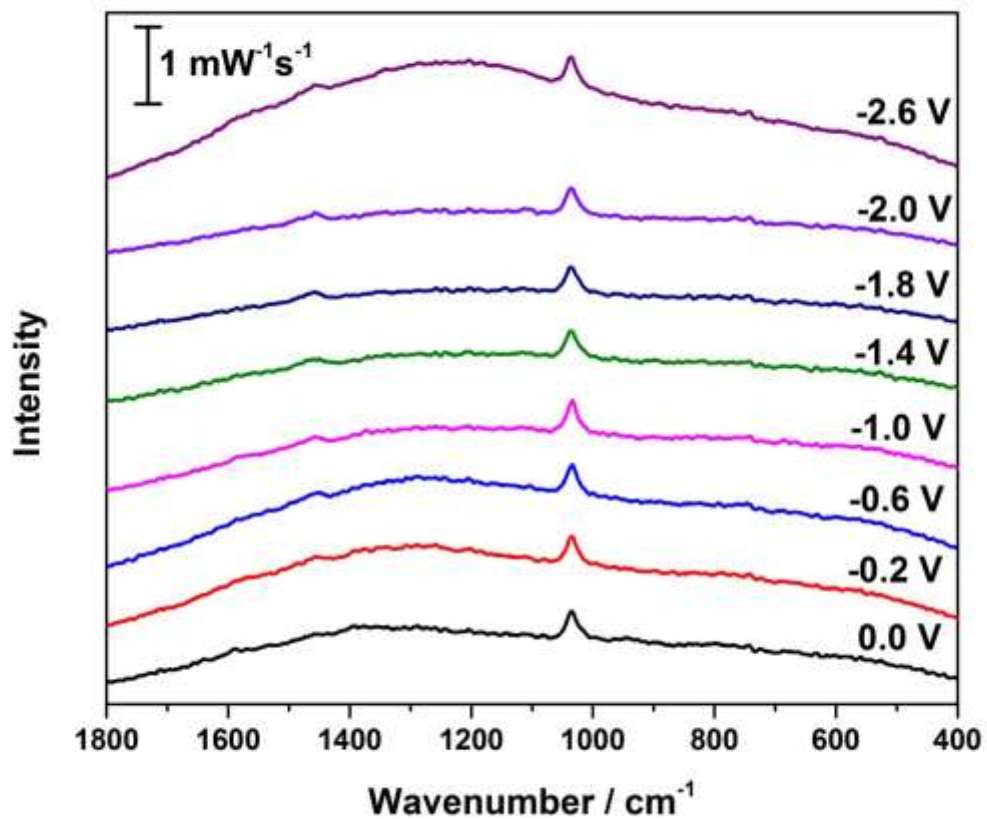
Figure S7. E-SERS spectra for the 0.1 M methanolic solution of 3-(carboxy)-1-methylpyridinium bis(trifluoromethanesulfonyl)imide IL. Collection time for each spectrum 30s, 55.9 mW.

Table S1: Summary of the bands observed for SERS of the 0.1M isobutyl IL methanolic solution at -1.6 V and the theoretical calculated gas phase bands for the isobutyl cation. An assignment is given for each band.

Experimental SERS / cm^{-1}	Calculated / cm^{-1}	Assignment
1730	1798	C=O ester stretching
1638	1665	C=C ring and C-H in plane deformation
1589	1622	C=C ring and C-H in plane deformation
-	1491	methyl asymmetric deformation
1469	-	pyridinium methyl symmetric deformation
-	1452	methyl deformation symmetric
-	1403	C-H(α) wag
1297	1305	ring breathing mode and C-CO$_2$ stretch
1204	1208	in-plane C-H deformation and C(α) - C(β) stretch
1033	1046	pyridinium in-plane ring breathing vibration
	994	C(γ) Me rock symmetric and C(α) -C(β) stretch
981	982	CH out of plane deformation (4+5-6)
-	970	C(β) -C(γ) antisymmetric stretch + C(γ) Me rock antisymmetric
-	929	ring deformation + N-C(Me) stretch
-	906	O-C(α) stretch
817	829	Out-of-plane ring breathing and C-O-C bend and N-C(Me) stretch and C(β) -C(γ) symmetric stretch
741	758	CCO$_2$ out of plane bend
690	700	In or Out-of-plane ring breathing vibrations
665		?
559		?
	543	in plane ring deformation
	477	N-CH3 in plane deformation
466	-	?
408	407	C-C bend ($\beta + \gamma$)
	346	C(3)-CO2 stretch

Table S2: DFT calculated band assignments for 3-(*n*-butoxycarbonyl)-1-methylpyridinium ion.

Frequency (cm^{-1})	Assignment
27	C(α) -O twist
40	O=C-OR twist
45	Me twist
59	C-CO$_2$ twist
68	C($\alpha\beta$) torsion
110	C($\beta\gamma$) torsion
134	C(3) in plane bend
152	C(3) out of plane bend
205	N-Me bend out of plane
217	C-C bend (β - γ)
243	C($\gamma\delta$) torsion
279	COC bend
308	N-Me bend in plane + C(3) in plane bend
365	N-Me bend in plane + CCO$_2$ in plane bend
407	C-C bend (β + γ)
422	ring out of plane deformation
446	N-Me bend in plane
479	ring out of plane deformation
513	ring in plane deformation
556	ring in plane deformation
677	ring out of plane deformation
702	ring in plane deformation
747	CH$_2$ rock
756	CCO$_2$ out of plane deformation + CH out of plane deformation
782	CH$_2$ rock
824	CH$_2$ rock
841	CH out of plane deformation (4 + 5 + 6)
889	ring in plane def + C(α)-O
913	C-C stretch ($\beta\gamma$ + $\gamma\delta$)
935	ring in plane def + C(α)-O
946	CH(2) out of plane deformation
966	CH$_2$ twist (α + β+ γ + δ)
982	CH out of plane deformation (2*6 -4 -5)
1025	C-C stretch ($\alpha\beta$ – $\gamma\delta$)
1038	CH out of plane deformation (4-5)
1046	ring in plane deformation
1057	C-C stretch ($\alpha\beta$ – $\beta\gamma$ + $\gamma\delta$)
1086	Me rock
1128	HCC in plane deformation + C(4)-C(5) stretch
1135	HCC in plane deformation + C(4)-C(5) stretch
1147	Me rock
1155	HCC in plane deformation
1194	HCC in plane deformation + CH$_2$ rock
1205	HCC in plane deformation
1222	HCC in plane deformation
1270	CH$_2$ twist (α + β+ γ)
1294	CH$_2$ wag (α + β+ γ)
1307	CH$_2$ wag (β+ γ)
1334	CH$_2$ twist (α - γ)
1336	CH$_2$ twist (α - β+ γ)

1339	HCC in plane deformation + N-C stretch
1348	HCC in plane deformation
1388	CH_2 wag ($\alpha + \beta - \gamma$)
1416	CH_2 wag ($\alpha - \beta$)+ Me symmetric deformation
1423	HCH (δ) symmetric deformation
1452	Me symmetric deformation
1478	Me deformation
1490	Me deformation
1490	CH_2 scissor ($2\alpha + \beta - \gamma - \delta$)
1492	CH_2 scissor ($\alpha + 2\beta + 2\gamma + \delta$)
1500	CH_2 scissor ($\alpha - \beta + 2\delta$)
1502	HCH (δ) deformation
1503	HCC in plane + Me deformations
1514	CH_2 scissor ($\alpha - \beta + \gamma - \delta$)
1531	HCC in plane + Me deformations
1622	C(3)-C(4) + C(6)-N stretch
1665	C(2)-C(3) + C(5)-C(6) stretch
1798	C=O stretch
3015	C-H (γ) symmetric
3026	C-H (δ) (1,1,1) symmetric - C-H (β) symmetric
3030	C-H (δ) (1,1,1) symmetric + C-H (β) symmetric
3042	C-H (γ) antisymmetric+ mixing from C-H (β)
3070	C-H (β) antisymmetric + mixing from C-H (γ)
3071	C-H (Me) symmetric
3086	C-H (α) symmetric
3091	C-H (δ) (0,1,-1) antisymmetric + mixing from C-H (β) and C-H (γ)
3102	C-H (δ) (0,1,-1) antisymmetric
3145	C-H (α) antisymmetric
3155	C-H (Me) (2,-1,-1) antisymmetric
3177	C-H (Me) (0,1,-1) antisymmetric
3203	C-H(4) stretch
3215	C-H(5) - C-H(6) stretch
3226	C-H(5) + C-H(6) stretch
3236	C-H(2) stretch

Table S3: DFT calculated band assignments for 3-(isobutoxycarbonyl)-1-methylpyridinium ion.

Frequency (cm^{-1})	Assignment
20	O-C(α) twist
43	Me twist
52	C-CO2 twist + O-C(α) twist
63	C-CO2 twist + O-C(α) twist
66	deformation
131	C(α)-C(β) torsion
172	CC(α)O deformation
203	out of plane deformation
213	C-CO2 twist + C(α)-C(β) torsion
226	C(γ) Me twist antisymmetric
245	C(γ) Me twist symmetric
250	COC bend
346	C(3)-CO2 stretch
368	N-Me in plane deformation + OC(O)C in plane deformation
372	O-C(α) and C(α)-C(β) torsion
381	CCC deformation symmetric
421	out-of-plane ring deformation
475	out-of-plane ring deformation
478	N-Me in plane deformation
543	in plane ring deformation
586	CCC deformation symmetric + OCC deformation
678	out-of-plane ring deformation
700	in plane ring deformation
758	CCO$_2$ out of plane bend
782	C(α) -C(β) symmetric stretch + C(β) -C(γ) symmetric stretch
829	C-O-C bend + N-C(Me) stretch + C(β) -C(γ) symmetric stretch
842	CH out of plane deformation (5+6)
905	O-C(α) stretch
912	C(γ) Me rock antisymmetric + CH$_2$(α) rock
930	ring deformation + N-C(Me) stretch
945	CH out of plane deformation (2)
949	C(γ) Me rock antisymmetric + CH$_2$(α) rock
970	C(β) -C(γ) antisymmetric stretch + C(γ) Me rock antisymmetric
982	CH out of plane deformation (4+5-6)
993	C(γ) Me rock symmetric + C(α) -C(β) stretch
1039	CH out of plane deformation (5-6)
1046	ring deformation in plane
1086	HCC in plane deformation + Me rock
1119	C(γ) Me rock symmetric
1137	HCC in plane deformation + Me rock
1147	Me rock
1159	HCC in plane deformation
1163	C(β) -C(γ) antisymmetric stretch
1204	HCC in plane deformation + N-C(Me) stretch
1209	C(α) -C(β) stretch
1222	HCC in plane deformation
1277	C-H(α) twist
1305	C-CO$_2$ stretch
1337	HCC in plane deformation + ring C-C,C-N stretch
1347	HCC in plane deformation+ ring C-C,C-N stretch

1360	C-H(β) wag
1369	C-H(β) wag
1403	C-H(α) wag
1405	C-H (γ) symmetric deformation antisymmetric
1433	C-H (γ) symmetric deformation symmetric
1452	Me deformation symmetric
1477	Me deformation antisymmetric
1488	C-H (γ) deformation antisymmetric
1490	Me deformation antisymmetric
1496	C-H (γ) deformation antisymmetric
1496	C-H(α) scissor
1504	Me deformation +HCC in plane
1510	C-H (γ) deformation symmetric
1513	C-H (γ) deformation symmetric
1531	HCC in plane + Me deformation
1622	C=C ring + C-H in plane deformation
1665	C=C ring + C-H in plane deformation
1797	C=O
3013	C-H (β) stretch
3026	C-H (γ) (1,1,1) antisymmetric stretch
3030	C-H (γ) (1,1,1) symmetric stretch
3068	C-H(α) symmetric stretch
3071	C-H (Me) (1,1,1) symmetric stretch
3085	C-H(γ) (0,1,-1) antisymmetric stretch
3090	C-H(γ) (0,1,-1) symmetric stretch
3101	C-H(γ) (2,-1,-1) antisymmetric stretch
3104	C-H(γ) (2,-1,-1) symmetric stretch
3121	C-H(α) antisymmetric stretch
3156	C-H (Me) (2,-1,-1) antisymmetric stretch
3176	C-H (Me) (0,1,-1) antisymmetric stretch
3203	C-H(4) stretch
3214	C-H(5) - C-H(6) stretch
3227	C-H(5) + C-H(6) stretch
3237	C-H(2) stretch

Table S4: DFT calculated band assignments for 3-(*sec*-butoxycarbonyl)-1-methylpyridinium ion.

Frequency (cm^{-1})	Assignment
33	O-C(α) torsion
46	NC(Me) torsion + C(O)-O torsion
49	NC(Me) torsion + C(O)-O torsion
78	C($\alpha\beta$') torsion + O-C(α) torsion
96	C-C(O$_2$) torsion
121	C($\alpha\beta$') torsion + CCCC(O$_2$) in plane deformation
162	CCCC(O$_2$) out of plane bend
190	CCO deformation + C(γ) torsion
205	ring out of plane deformation
216	C($\alpha\beta$) - C($\beta\gamma$) torsion
253	C($\alpha\beta$) + C($\beta\gamma$) torsion
270	C(β')-C(α)-C(β) bend + C(α)-C(β)-C(γ) bend
296	CCC(O$_2$) in plane bend
366	CNC(Me) in plane bend + O=CC bend
388	C(β')-C(α)-C(β) + CCO bend
414	C(β')-C(α)-C(β) bend
429	CNC(Me) out of plane bend
474	CNC(Me) in plane bend
482	ring out of plane deformation
525	ring in plane deformation
561	ring in plane deformation
678	ring out of plane deformation
708	ring in plane deformation
758	CCO$_2$ out of plane bend
772	O-C(α) stretch+ C-H(α) stretch + C-H(β) stretch
806	CH$_2$ rock
813	C-O-C deformation
842	C-H out of plane deformation (4+5+6)
872	C(α)-C(β) + C(α)-C(β') + C(β')-C(γ) stretch
923	ring in plane deformation
948	C-H out of plane deformation (2)
970	C(α)-C(β) + C(α)-C(β') + C(β')-C(γ) stretch
982	C-H out of plane deformation (4+5-6)
996	C-H(β) rock + CH$_2$ twist +C-H(α) def
1027	C(α)-C(β) + C(α)-C(β') + C(β')-C(γ) stretch
1039	C-H out of plane deformation (4-5)
1046	ring in plane deformation
1085	C(Me) rock
1111	O-C(α) + C-H(β) rock + C-H(γ) rock
1132	CH in plane deformation
1147	C(Me) rock
1155	CH in plane deformation
1166	C(α)-C(β) – C(α)-C(β') stretch
1200	C-H(β) rock + C-H(γ) rock
1202	C-H(β) rock - C-H(γ) rock
1221	CH in plane deformation
1295	C-C(O2) stretch – CO stretch
1302	CH$_2$ twist
1336	CH in plane deformation

1345	CH in plane deformation
1349	CH_2 wag
1391	C-H(α) deformation
1406	C-H(α) deformation
1418	C-H(β) symmetric deformation - C-H(γ) symmetric deformation
1424	C-H(β) symmetric deformation + C-H(γ) symmetric deformation
1452	C(Me) symmetric deformation
1477	C(Me) deformation
1490	C(Me) deformation
1491	CH_2 scissor + C-H(β) deformation + C-H(γ) deformation
1494	CH_2 scissor + C-H(β) deformation + C-H(γ) deformation
1502	C-H(β) deformation + C-H(γ) deformation
1505	C(Me) deformation + C-H in plane deformation (4,5)
1509	C-H(β) deformation + C-H(γ) deformation
1515	CH_2 scissor + C-H(β) deformation + C-H(γ) deformation
1530	C(Me) deformation + C-H in plane deformation
1622	ring stretch (5-6 – 6-1) + C-H in plane deformation
1664	ring stretch (1-2 + 4-5) + C-H in plane deformation
1792	C=O stretch
3033	C-H(γ) (1,1,1) symmetric stretch + C-H(β') symmetric stretch
3035	C-H(γ) (1,1,1) symmetric stretch - C-H(β') symmetric stretch
3048	C-H(β) (1,1,1) symmetric stretch
3071	C-H(Me) symmetric stretch
3075	C-H(α) stretch + C-H(β') antiperiplanar stretch
3088	C-H(β') antisymmetric stretch+ C-H(γ) (0,1,-1) antisymmetric stretch +C-H(α)
3106	C-H(β') antisymmetric stretch+ C-H(γ) (0,1,-1) antisymmetric stretch
3109	C-H(β) (0,1,-1) - C-H(γ) (0,1,-1) antisymmetric stretch
3113	C-H(β) (0,1,-1) + C-H(γ) (0,1,-1) antisymmetric stretch
3136	C-H(β) (2,1,1) antisymmetric stretch
3156	C-H(Me) (2,1,1) antisymmetric stretch
3176	C-H(Me) (0,1,-1) antisymmetric stretch
3203	C-H(6) stretch
3216	C-H(4) - C-H(5) stretch
3227	C-H(4) + C-H(5) stretch
3238	C-H(2) stretch

Table S5: DFT calculated band assignments for 3-(*tert*-butoxycarbonyl)-1-methylpyridinium ion.

Frequency (cm^{-1})	Assignment
19	N-C(Me) twist
33	N-C(Me) twist + C(O)-O twist + O-C(α) twist
52	N-C(Me) twist + C(O)-O twist
88	COC(α) deformation +CC(O)O bend
108	C-C(O$_2$) torsion + OC(α) torsion
168	C(α) rock + CCCC out of plane deformation
201	C(α) rock
205	CH$_3$(β) twist + NMe out of plane deformation
207	CH$_3$(β) twist
254	CH$_3$(β) twist
269	CH$_3$(β) twist
275	CCC(O$_2$) in plane bend + C(α) deformation
321	C(α) deformation
346	C(α) deformation
365	CNC(Me) in plane deformation +CC(O)O bend
412	CNC(Me) in plane deformation +OC(α)C bend
417	ring out of plane deformation
447	OC(α)C bend
458	OC(α)C bend
485	ring out of plane deformation + OC(α)C bend
494	CNC(Me) in plane deformation +OC(α)C bend
544	ring in plane deformation
678	ring out of plane deformation
691	C-O stretch + ring in plane deformation
733	C-O stretch + ring in plane deformation
759	CCO$_2$ out of plane bend
805	C-O + C(α) -C(β) stretch
825	COC deformation
842	HCC out of plane deformation (4+5+6)
925	CH$_3$(β) rock
927	CH$_3$(β) rock
933	CH$_3$(β) rock
947	HCC out of plane deformation (6)
976	CH$_3$(β) rock
982	HCC out of plane deformation (4+5-6)
1039	HCC out of plane deformation (4-5)
1046	ring in plane deformation
1052	CH$_3$(β) rock
1055	CH$_3$(β) rock
1085	HCC in plane deformation (4) + CH$_3$(Me) rock
1133	HCC in plane deformation (3,4)
1147	CH$_3$(Me) rock
1155	HCC in plane deformation (3,6) + CH$_3$(Me) rock
1170	HCC in plane deformation (3,6) + CH$_3$(β) rock
1209	HCC in plane deformation
1225	HCC in plane deformation + N-C stretch
1273	C(α) -C(β') - C(α) -C(β'') stretch
1285	C(α) -C(β) stretch + COC bend
1314	C-C(O$_2$) stretch + C-O stretch

1337	HCC in plane deformation + N-C stretch
1345	HCC in plane deformation
1408	C-H(β) + C-H(β') + C-H(β'') symmetric deformation
1409	C-H(β) + C-H(β') + C-H(β'') symmetric deformation
1434	C-H(β) + C-H(β') + C-H(β'') symmetric deformation
1452	C(Me) symmetric deformation
1473	C-H(β) + C-H(β') + C-H(β'') deformation
1477	C(Me) deformation
1487	C-H(β) + C-H(β') + C-H(β'') deformation
1489	C(Me) deformation
1492	C-H(β) + C-H(β') + C-H(β'') deformation
1501	C-H(β') + C-H(β'') deformation
1504	C-H(β) + C-H(β') + C-H(β'') deformation
1505	C(Me) deformation + HCC in plane deformation
1524	C-H(β) + C-H(β') + C-H(β'') deformation
1529	C(Me) deformation + HCC in plane deformation
1621	ring stretch + HCC in plane deformation
1664	ring stretch + HCC in plane deformation
1788	C=O stretch
3040	2*C-H(β) - C-H(β') - C-H(β'') (1,1,1) symmetric stretch
3043	C-H(β') - C-H(β'') (1,1,1) symmetric stretch
3049	C-H(β) + C-H(β') + C-H(β'') (1,1,1) symmetric stretch
3070	C-H(Me) symmetric stretch
3105	C-H(β') (0,1,-1) - C-H(β'') (0,1,-1) antisymmetric stretch
3107	C-H(β') (0,1,-1) + C-H(β'') (0,1,-1) antisymmetric stretch
3112	C-H(β) (0,1,-1) antisymmetric stretch
3119	C-H(β) (2,1,1) antisymmetric stretch
3138	C-H(β') (2,1,1) - C-H(β'') (2,1,1) antisymmetric stretch
3142	C-H(β') (2,1,1) + C-H(β'') (2,1,1) antisymmetric stretch
3155	C-H(Me) (2,1,1) antisymmetric stretch
3175	C-H(Me) (0,1,-1) antisymmetric stretch
3203	C-H(6) stretch
3215	C-H(4) - C-H(5) stretch
3227	C-H(4) + C-H(5) stretch
3237	C-H(2) stretch