Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Aromatic heterocyclic anion based ionic liquids and electrolytes

Mukhtiar Ahmed[1], Soniya S. Rao[2], Andrei Filippov[1], Patrik Johansson[2*], and Faiz Ullah Shah[1*]

[1]Chemistry of Interfaces, Luleå University of Technology, SE-971 87 Luleå, Sweden

[2]Department of Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

[*]Corresponding authors:

patrik.johansson@chalmers.se

faiz.ullah@ltu.se

Synthesis and Characterization

(P_{4444})(3-PyrA): Transparent yellowish room temperature liquid. MS (ESI). $[C_{16}H_{36}P]^+$: Calcd m/z 259.2556. Found m/z 259.2555, $[C_6H_4NO_2]^-$: Calcd m/z 122.0247, Found m/z 122.0222. ^{1}H NMR (400.21 MHz, $CDCl_3$), $^\delta$(ppm): 9.19-9.20 (m, 1H), 8.47-8.49 (m, 1H), 8.28-8.21 (m, 1H),7.17-7.20 (m, 1H), 2.31-2.36 (m, 8H, P-CH_2-), 1.42-1.51 (m, 16H, -CH_2-), 0.93-0.96 (t, $3J_{HH}$ = 7.1 Hz, 12H, -CH_3) ppm. ^{13}C NMR (100.64 MHz, $CDCl_3$): 169.88, 151.33, 149.58, 136.97, 135.52, 122.60, 24.17, 24.02, 23.93, 23.88, 19.05, 18.58, 13.56 ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$): 33.12 ppm.

(P_{4444})(4-PyrA): White solid, MS (ESI). $[C_{16}H_{36}P]^+$: Calcd m/z 259.2556. Found m/z 259.2562, $[C_6H_4NO_2]^-$: Calcd m/z 122.0247. Found m/z 122.0188.^{1}H NMR (400.21 MHz, $CDCl_3$), $^\delta$(ppm): 8.52-8.54 (m, 2H), 7.82-7.84 (m, 2H), 2.29-2.36 (m, 8H, P-CH_2-), 1.46-1.49 (m, 16H, -CH_2-), 0.90-0.93 (t, $3J_{HH}$ = 7.1 Hz, 12H, -CH_3) ppm. ^{13}C NMR (100.64 MHz, CDCl3): 169.77, 148.16, 123.72, 24.17, 24.02, 23.92, 23.87, 19.04, 18.58, 13.56 ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$): 33.10 ppm.

(P_{4444})(2-PyrA): Yellowish gel. MS (ESI). $[C_{16}H_{36}P]^+$: Calcd m/z 259.2556. Found m/z 259.2535, MS (ESI). $[C_6H_4NO_2]^-$: Calcd m/z 122.0247, Found m/z 122.0212. ^{1}H NMR (400.21 MHz, $CDCl_3$), $^\delta$(ppm): 8.36-8.37 (m, 1H), 7.90-7.92 (m, 1H), 7.42-7.45 (m, ^{1}H), 6.95-6.98 (m, 1H), 2.19-2.27 (m, 8H, P-CH_2-), 1.25-1.34 (m, 16H, -CH_2-), 0.72-0.74 (t, $3J_{HH}$ = 7.1 Hz, 12H, -CH_3) ppm. ^{13}C NMR (100.64 MHz, $CDCl_3$): 170.56, 158.10, 148.48, 135.74, 123.94, 123.10, 24.21,24.12, 24.06, 19.10, 18.63, 13.65 ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$): 33.08 ppm.

(P_{4444})(2,5-PyrA): Transparent yellow room temperature liquid. MS (ESI). $[C_{16}H_{36}P]^+$: Calcd m/z 259.2556. Found m/z 259.2562, MS (ESI). $[C_6H_4NO_2]^-$: Calcd m/z 123.0200, Found m/z 123.0146. ^{1}H NMR (400.21 MHz, $CDCl_3$), $^\delta$(ppm): 8.52-8.54 (m, 2H), 7.82-7.84 (m, 2H), 2.29-

2.36 (m, 8H, P-CH_2-), 1.46-1.49 (m, 16H, -CH_2-), 0.90-0.93 (t, $3J_{HH}$ = 7.1 Hz, 12H, -CH_3) ppm. ^{13}C NMR (100.64 MHz, $CDCl_3$): 168.78, 152.64, 146.21, 143.81, 143.39, 24.26, 24.10, 24.05, 19.17, 18.70, 13.65 ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$): 33.19 ppm.

(P_{4444})(Pyr-2,6-diA): White crystalline solid. MS (ESI). $[C_{16}H_{36}P]^+$: Calcd m/z 259.2556. Found m/z 259.2562, $[C_7H_3NO_4]^{2-}$: Calcd m/z 165.10412, Found m/z 166.0146. Found m/z 389.157. ^{1}H NMR (400.21 MHz, $CDCl_3$), $^{\delta}$(ppm): 8.09-8.11 (m, 2H), 7.59-7.61 (m, 1H), 2.21-2.27 (m, 16H, P-CH_2-), 1.36-1.37 (m, 32H, -CH_2-), 0.84-0.87 (t, $3J_{HH}$ = 7.1 Hz, 24H, -CH_3) ppm. ^{13}C NMR (100.64 MHz, $CDCl_3$): 170.39, 155.85, 135.85, 124.22, 24.02, 23.99, 23.95, 23.87, 18.93, 18.46, 13.65 ppm. ^{31}P NMR (162.01 MHz, $CDCl_3$): 32.80 ppm.

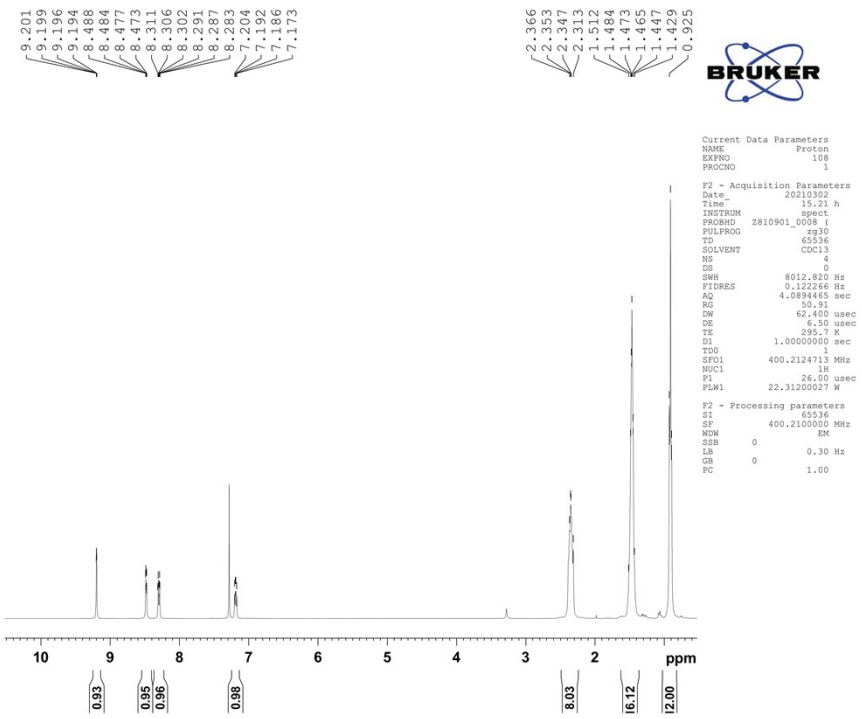


Figure S1. ^{1}H NMR spectrum of (P_{4444})(3-PyrA) in $CDCl_3$.

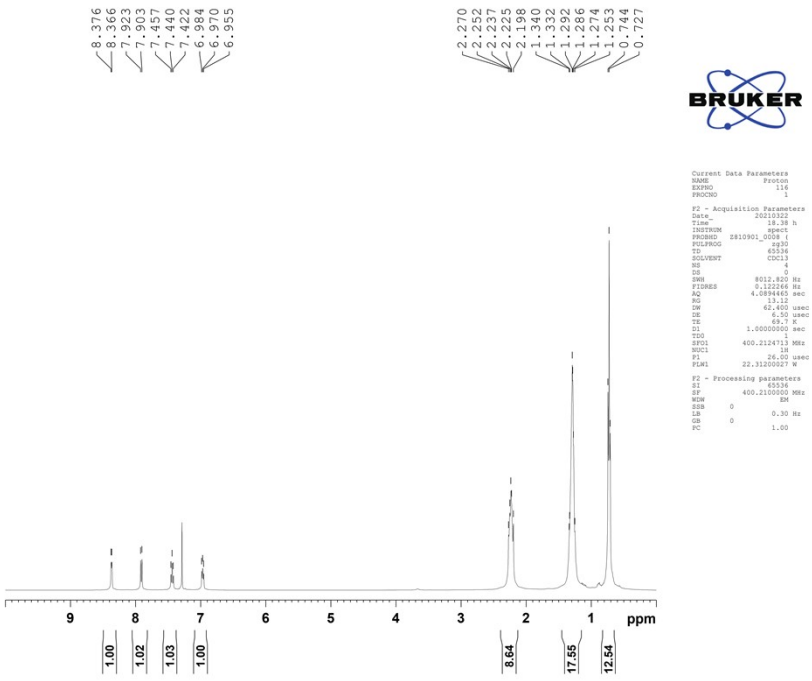


Figure S2. ^{1}H NMR spectrum of $(P_{4444})(2\text{-PyrA})$ in $CDCl_3$.

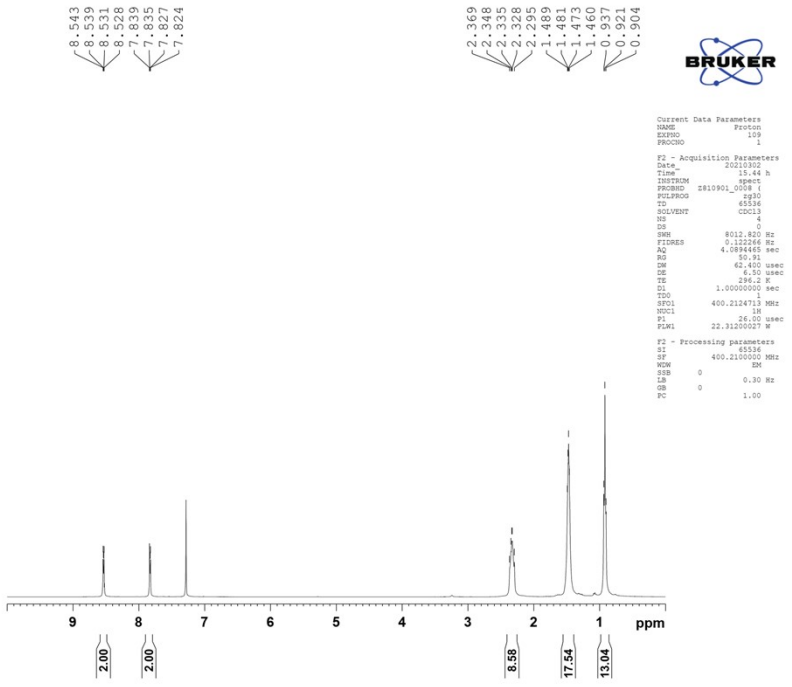


Figure S3. ^{1}H NMR spectrum of $(P_{4444})(4\text{-PyrA})$ in $CDCl_3$.

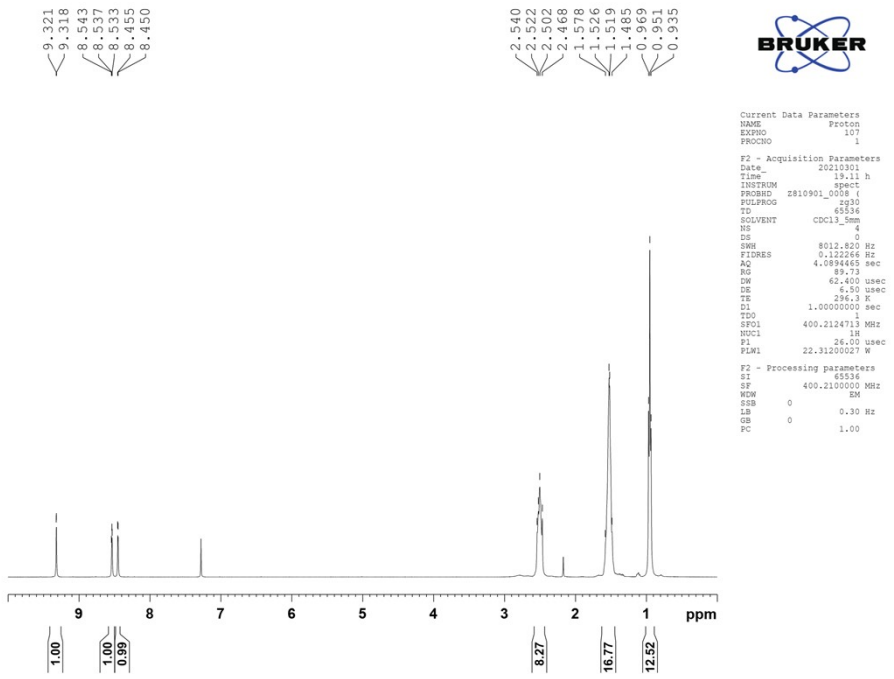


Figure S4. ^{1}H NMR spectrum of (P_{4444})(2,5-PyrA) in $CDCl_3$.

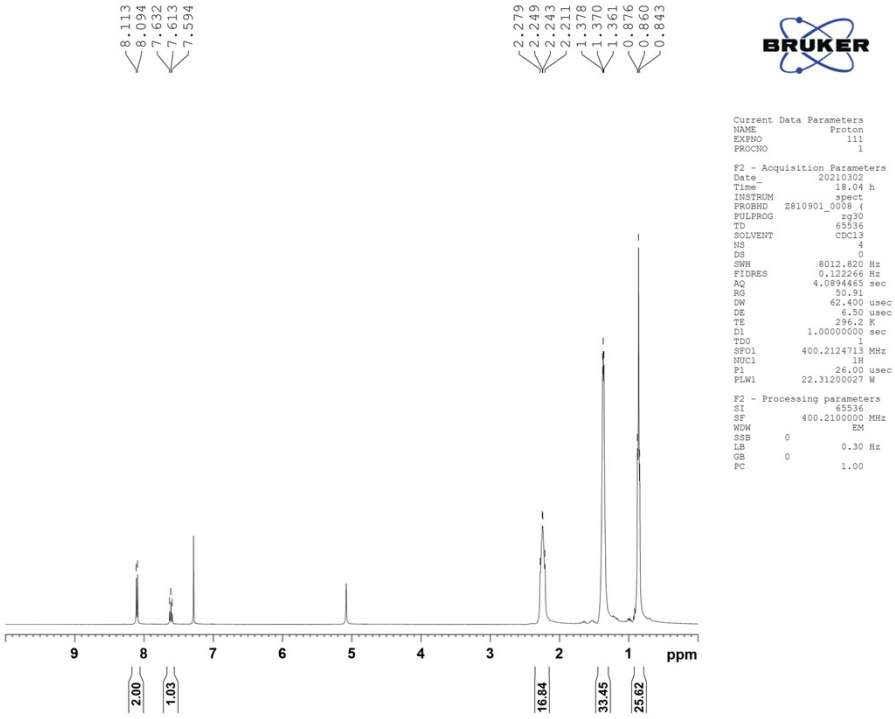


Figure S5. ^{1}H NMR spectrum of (P_{4444})(Pyr-2,6-diA) in $CDCl_3$.

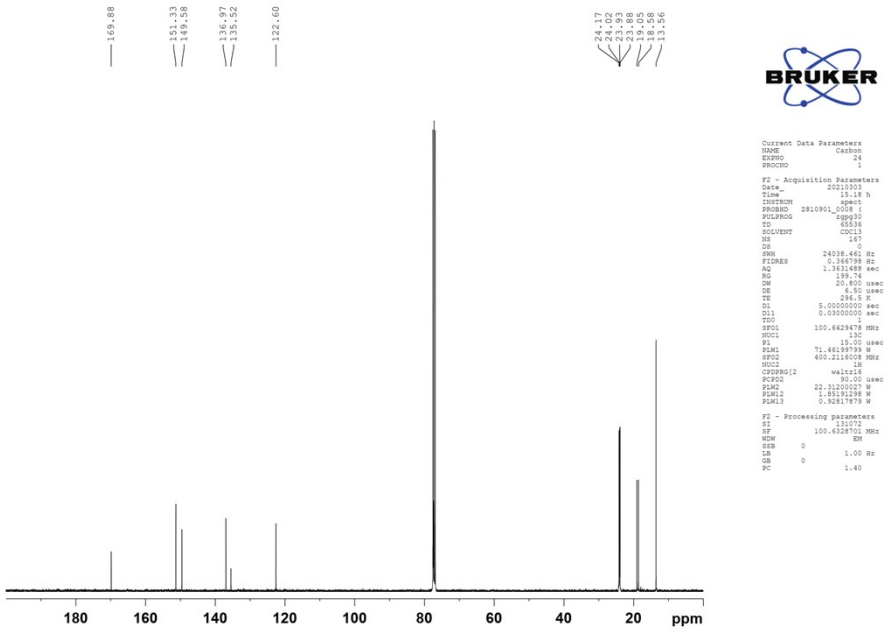


Figure S6. ^{13}C NMR spectrum of (P_{4444})(2-PyrA) in $CDCl_3$.

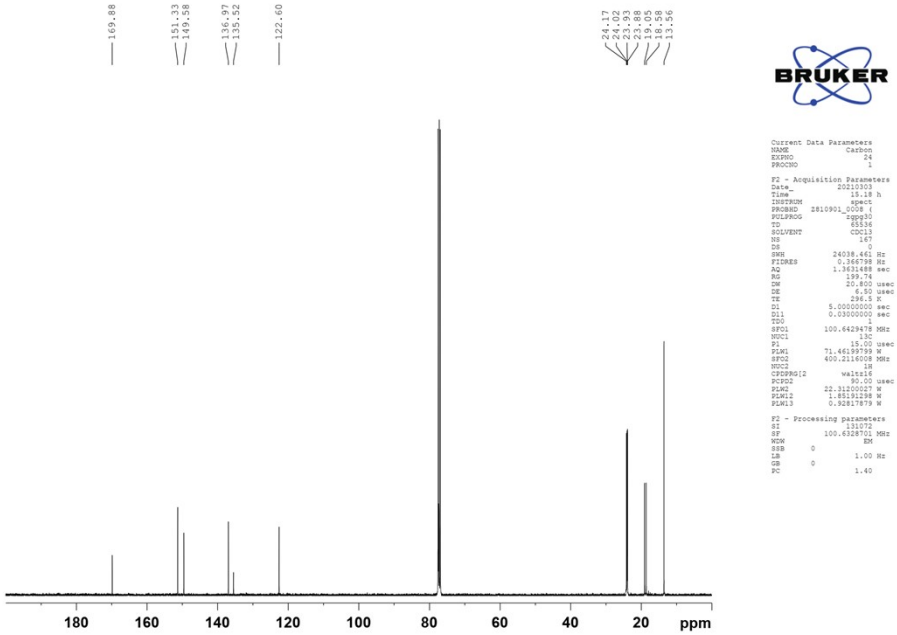


Figure S7. ^{13}C NMR spectrum of (P_{4444})(3-PyrA) in $CDCl_3$.

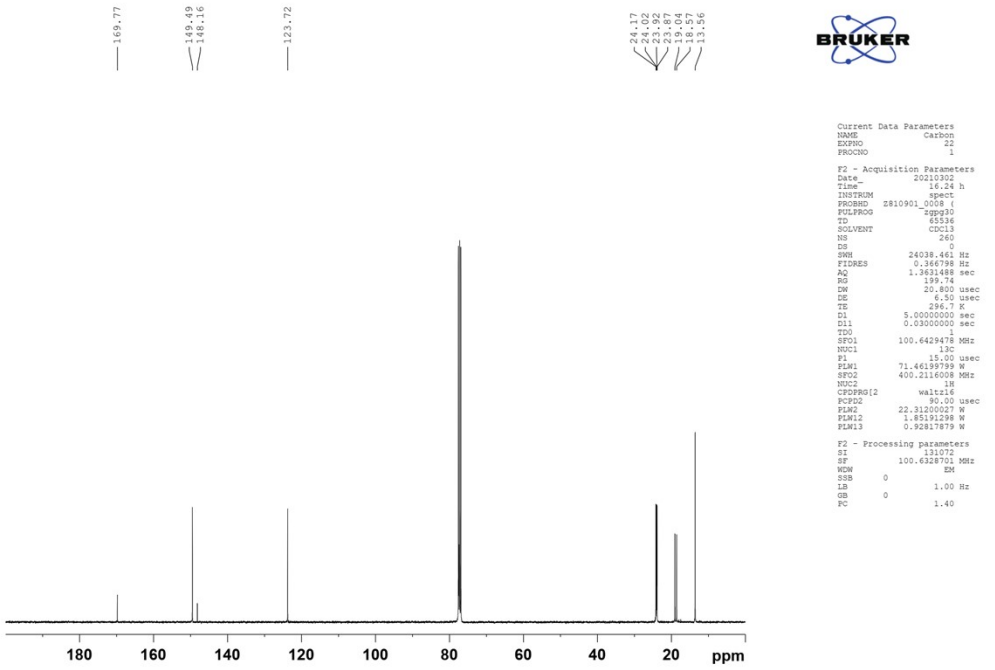


Figure S8. ^{13}C NMR spectrum of (P_{4444})(4-PyrA) in $CDCl_3$.

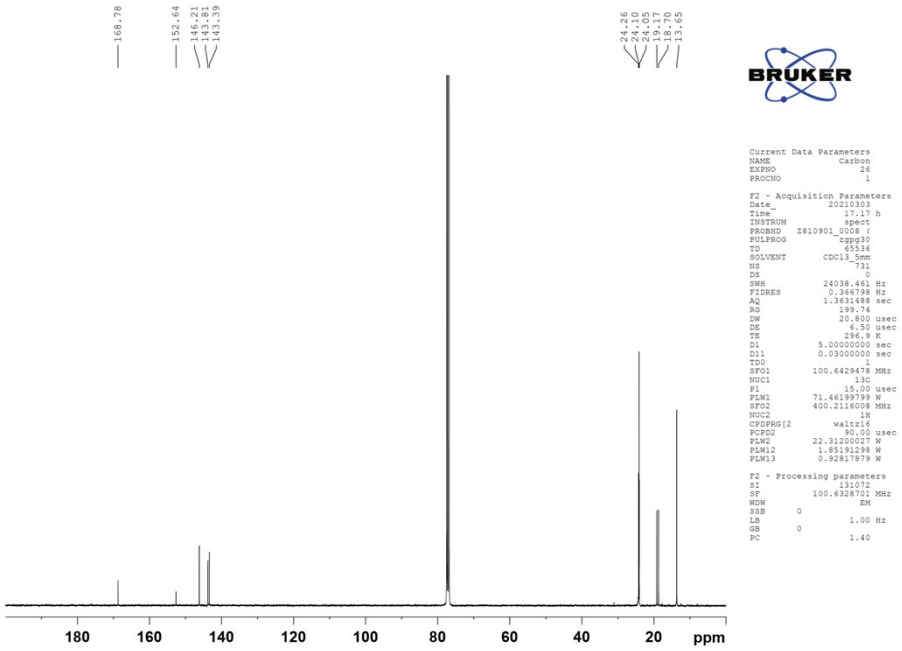


Figure S9. ^{13}C NMR spectrum of (P_{4444})(2,5-PyrA) in $CDCl_3$.

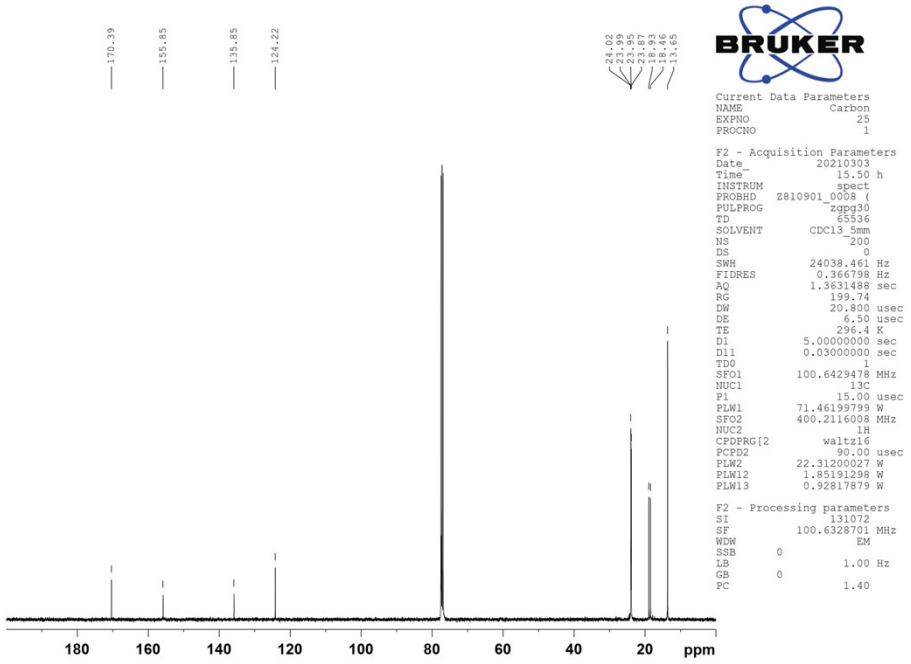


Figure S10. ^{13}C NMR spectrum of (P_{4444})(Pyr-2,6-diA) in $CDCl_3$.

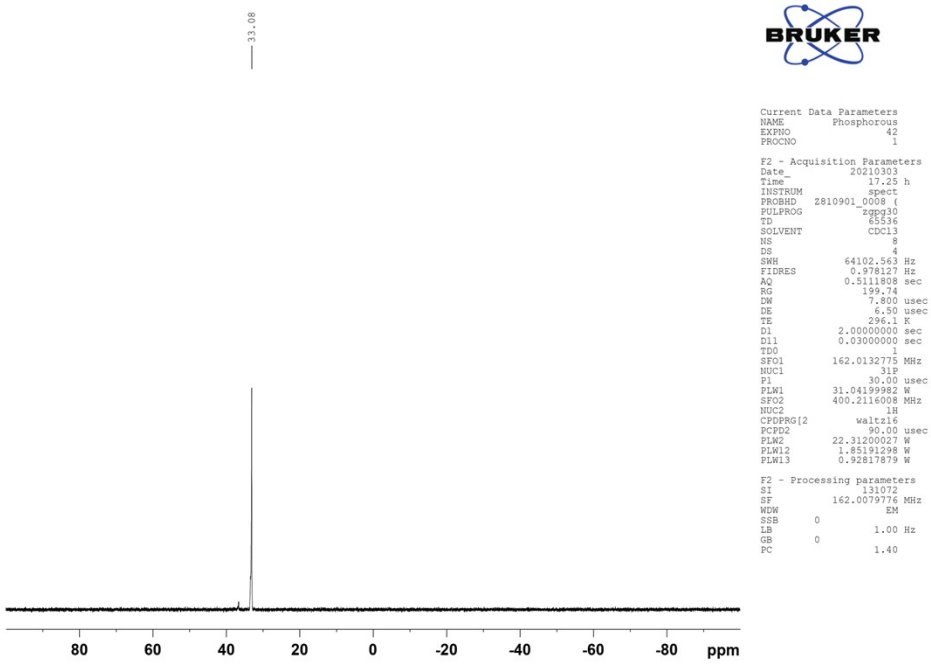


Figure S11. ^{31}P NMR spectrum of (P_{4444})(2-PyrA) in $CDCl_3$.

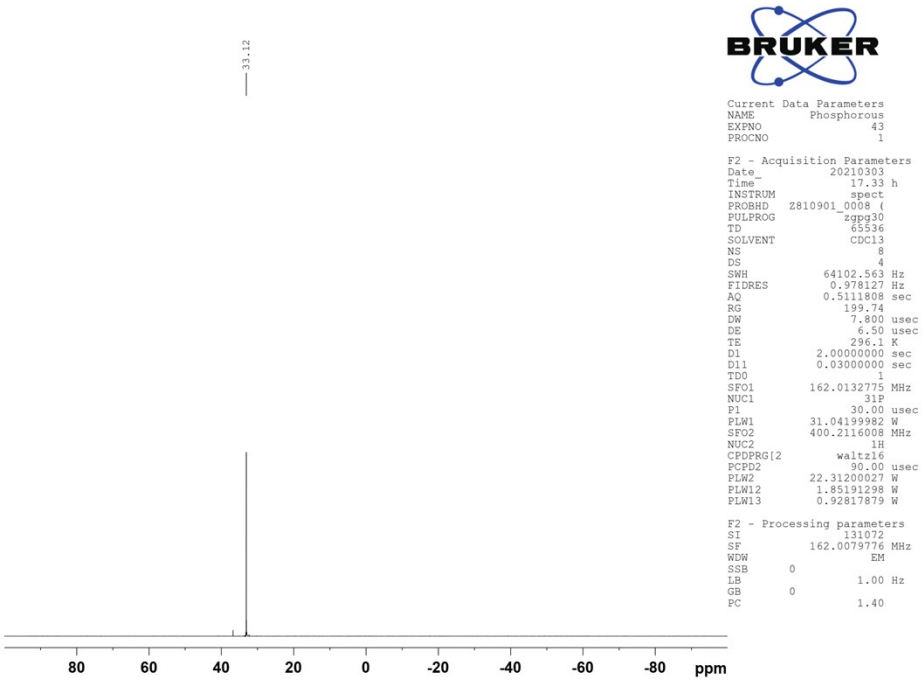


Figure S12. ^{31}P NMR spectrum of (P_{4444})(3-PyrA) in $CDCl_3$.

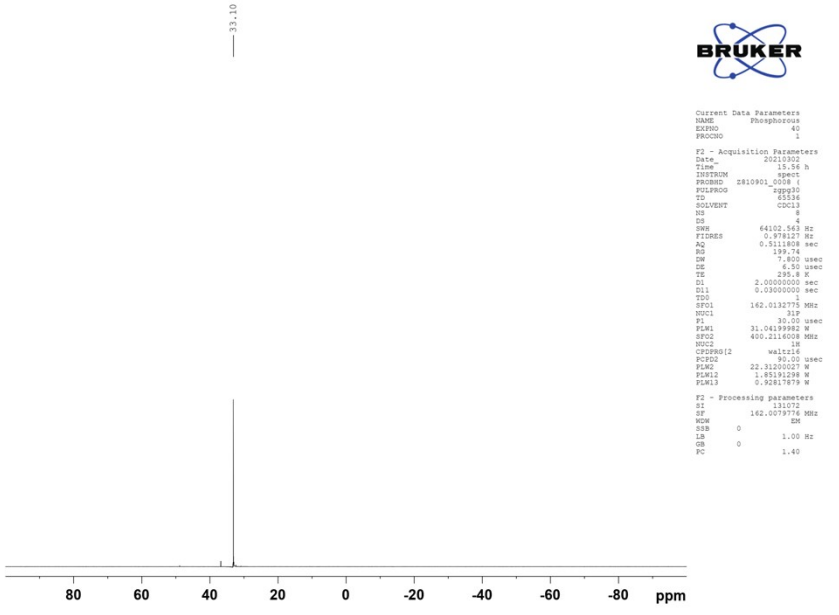


Figure S13. ^{31}P NMR spectrum of (P_{4444})(4-PyrA) in $CDCl_3$.

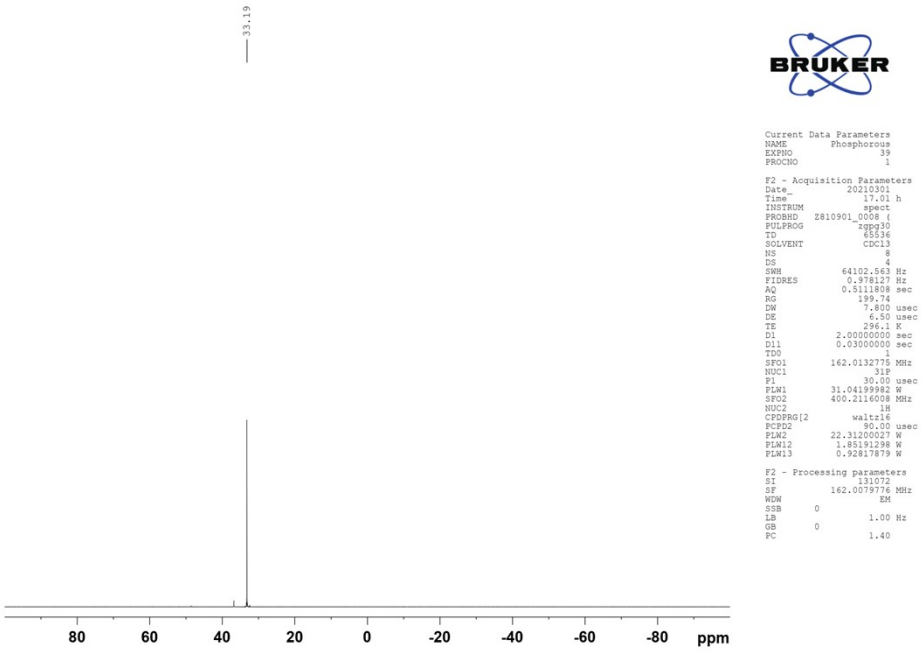


Figure S14. ^{31}P NMR spectrum of (P_{4444})(2,5-PyrA) in $CDCl_3$.

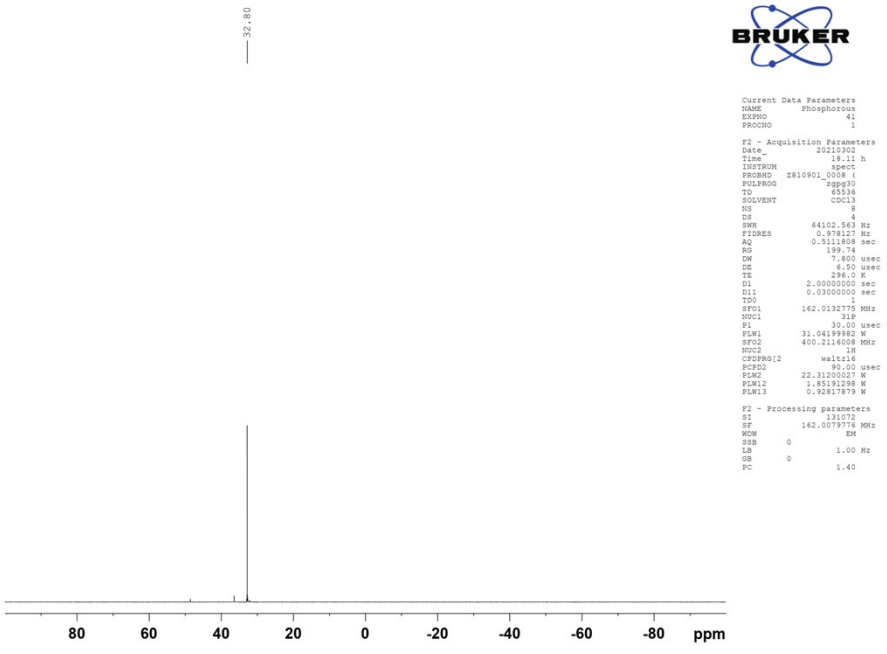


Figure S15. ^{31}P NMR spectrum of (P_{4444})(Pyr-2,6-diA) in $CDCl_3$.

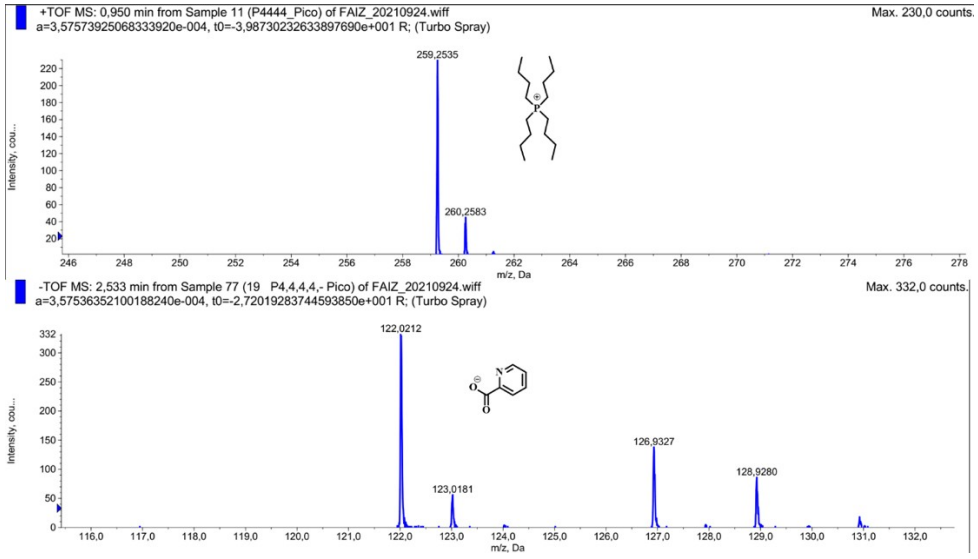


Figure S16. ESI-MS of (P_{4444})(2-PyrA)

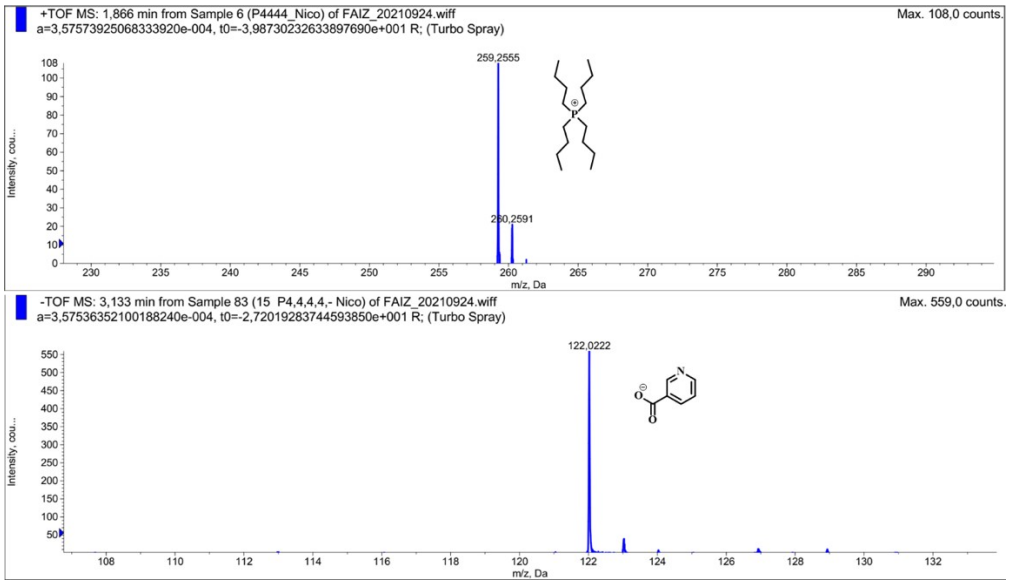


Figure S17. ESI-MS of (P_{4444})(3-PyrA)

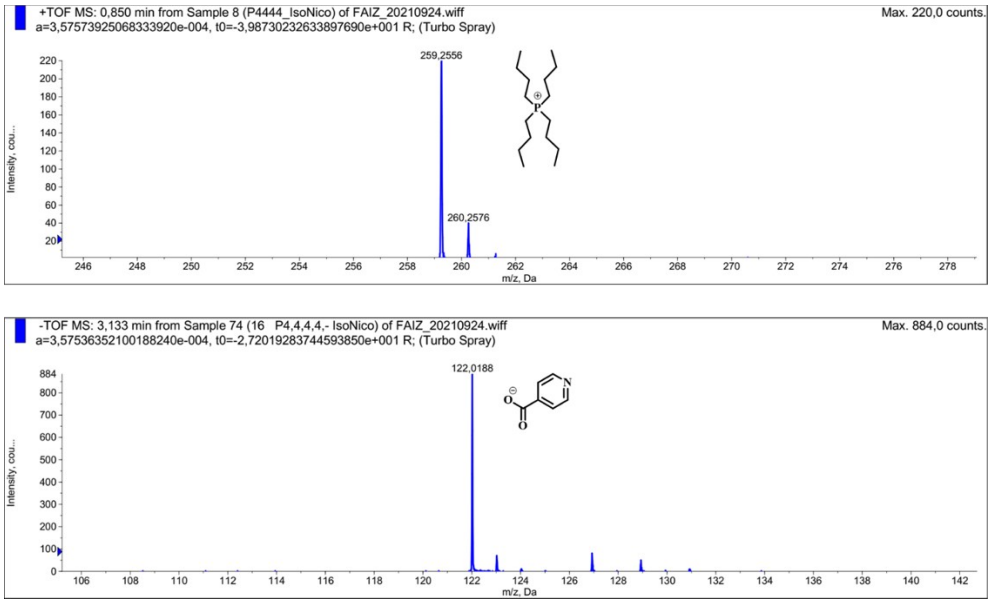


Figure S18. ESI-MS of (P_{4444})(4-PyrA)

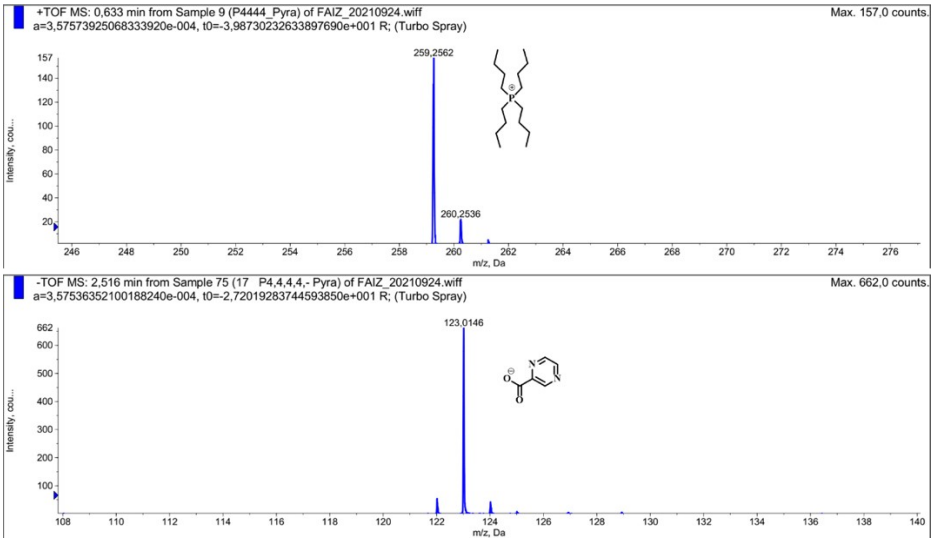


Figure S19. ESI-MS of (P_{4444})(2,6-PyrA)

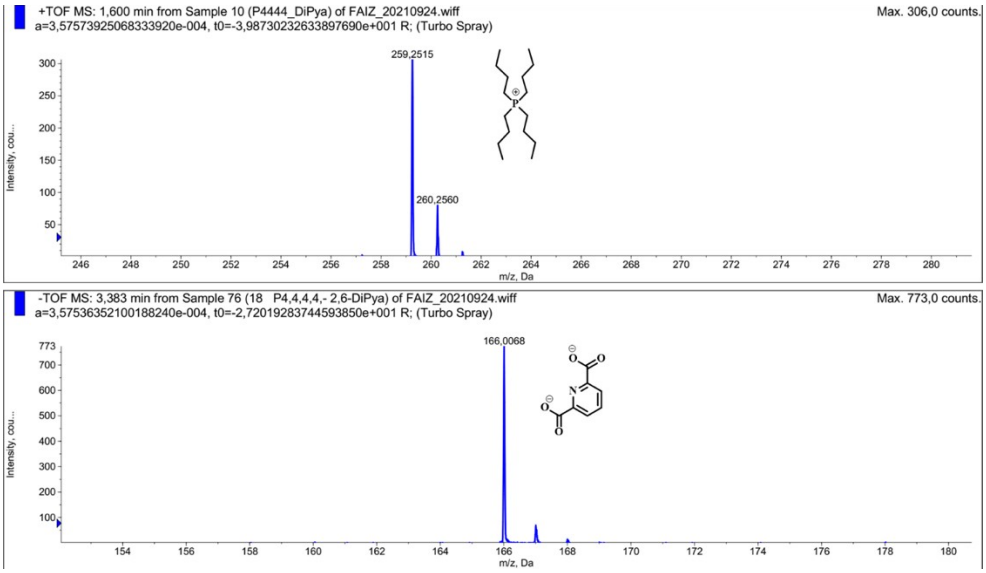


Figure S20. ESI-MS of (P_{4444})(Pyr-2,6-diA)

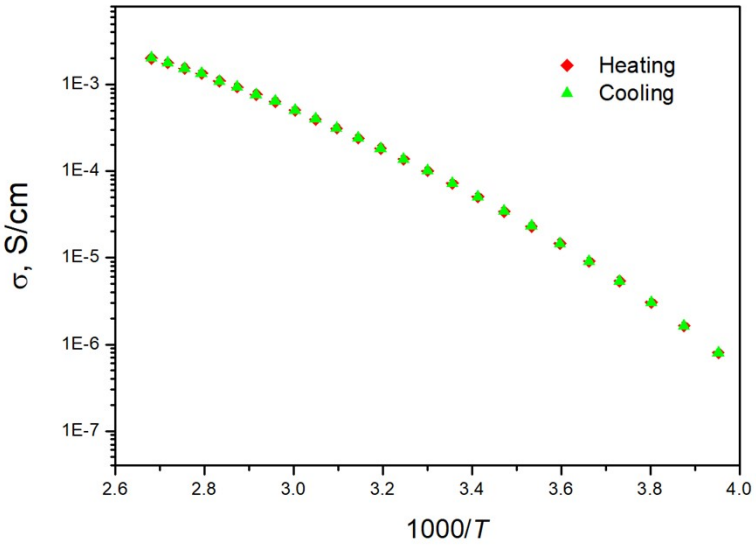


Figure S21. Heating and cooling cycles of the ionic conductivity of (P_{4444})(3-PyrA)

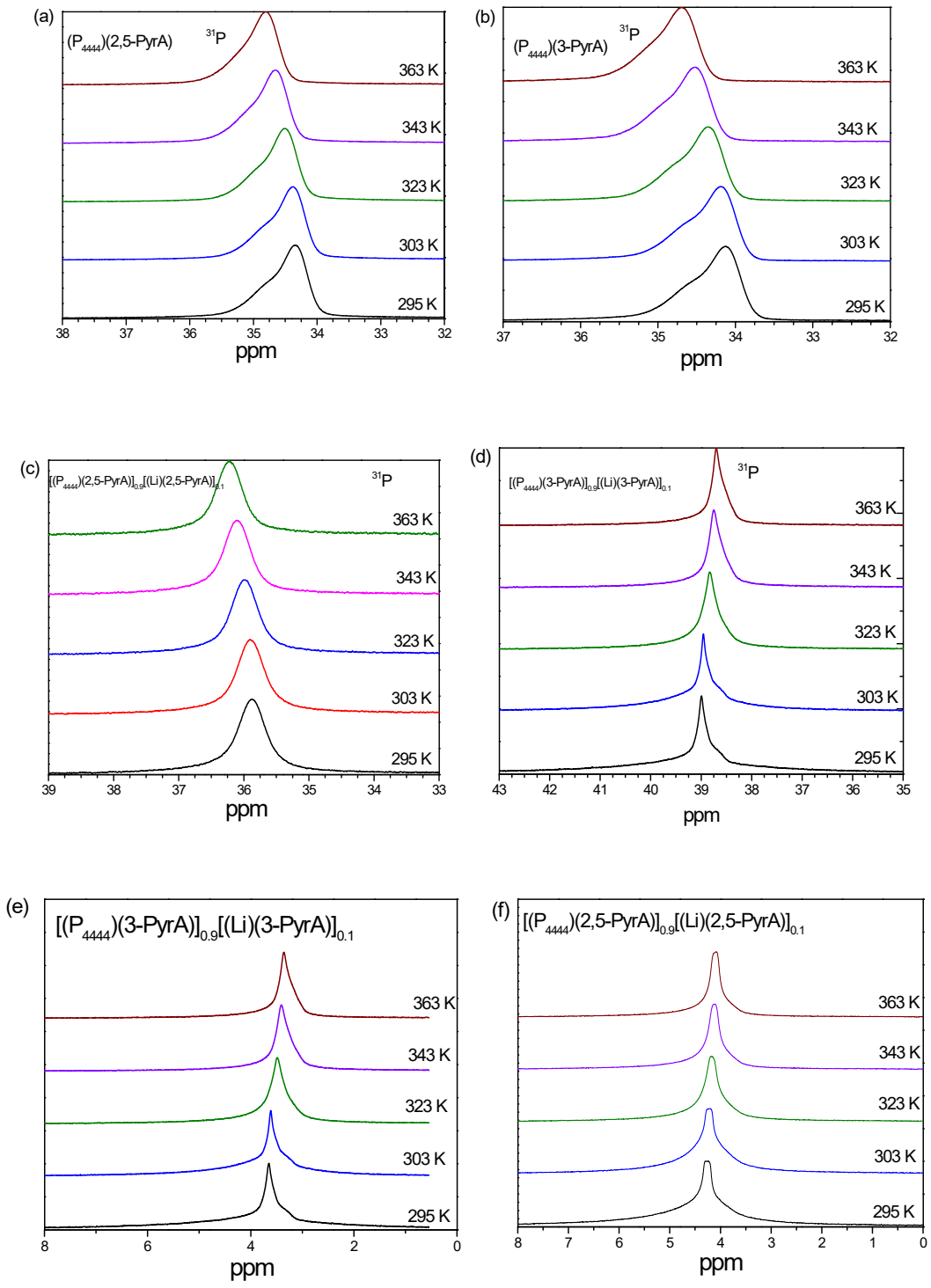
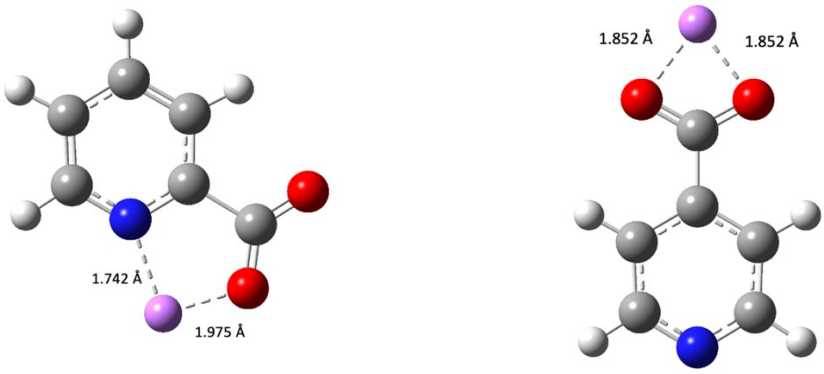


Figure S22. ^{31}P NMR spectra of (a) [(P_{4444})(2,5-PyrA)] (b) [(P_{4444})(3-PyrA)] (c) [(P_{4444})(2,5-PyrA)]$_{0.9}$[(Li)(2,5-PyrA)]$_{0.1}$ and (d) [(P_{4444})(3-PyrA)]$_{0.9}$[(Li)(3-PyrA)]$_{0.1}$ and ^{7}Li NMR (e) [(P_{4444})(3-PyrA)]$_{0.9}$[(Li)(3-PyrA)]$_{0.1}$ and (f) [(P_{4444})(2,5-PyrA)]$_{0.9}$[(Li)(2,5-PyrA)]$_{0.1}$ as a function of temperature.



(a) 2-PyrA (-709 kJ mol^{-1})

(b) 4-PyrA (-666 kJ mol^{-1})

Figure S23: Optimized geometries of the various Li^+–ion-pairs for: (a) $(2\text{-PyrA})^-$ and (b) $(4\text{-PyrA})^-$, and including coordination bond distances and association energies.

Table S1. VFT equation parameters and apparent activation energies for ionic conductivity of the ionic liquids and the electrolytes.

System	σ_0 mS/cm	B,K	T_0, K	$E\sigma$, kJ/(mol)
(P_{4444}) (3-PyrA)	1.218	1381	156	11.4
(P_{4444}) (2,5-PyrA)	0.135	1496	150	12.4
$[(P_{4444})(3\text{-PyrA})]_{0.9}$ $[Li(3\text{-PyrA})]_{0.1}$	2.352	1600	148	13.3
$[(P_{4444})$ (2,6-PyrA)$]_{0.9}$ $[Li(2,6\text{-PyrA})]_{0.1}$	0.216	1626	143	13.5

Table S2. VFT equation parameters and apparent activation energies for ion diffusivity of the ionic liquids and the electrolytes.

System	ion	$D_0 \times 10^{-8}$ m^2/s	B,K	T_0, K	E_D, kJ/(mol)
(P_{4444}) (3-PyrA)	$(3\text{-PyrA})^-$	1.55	800	213	6.7
	$(P_{4444})^+$	1.49	826	211	6.9
$[(P_{4444})(3\text{-PyrA})]_{0.9}$ $[Li(3\text{-PyrA})]_{0.1}$	$(3\text{-PyrA})^-$	5.07	1100	200	9.2
	$(P_{4444})^+$	3.36	1000	204	8.3
	Li^+	6.46	1124	205	9.3
(P_{4444}) (2,5-PyrA)	(2,6-PyrA)$^-$	1.53	853	210	7.1
	$(P_{4444})^+$	1.59	892	207	7.4
$[(P_{4444})$ (2,5-PyrA)$]_{0.9}$ $[Li(2,5\text{-PyrA})]_{0.1}$	(2,6-PyrA)$^-$	3.20	990	205	8.2
	$(P_{4444})^+$	3.03	998	205	8.3
	Li^+	3.50	1024	205	8.5

Table S3. Anodic and cathodic limits, and electrochemical stability windows (ESWs) of the neat ionic liquids and the electrolytes at 0.10 mA cm^{-2} cut-off current density using GC as WE at 293K *vs*. Li/Li^+.

System	E_A (V)	E_C (V)	ΔE (V)
(P_{4444}) (3-PyrA)	4.97	1.39	3.57
$[(P_{4444})(3\text{-PyrA})]_{0.9}$ $[Li(3\text{-PyrA})]_{0.1}$	5.03	1.29	3.74
(P_{4444}) (2,5-PyrA)	4.09	1.27	2.82
$[(P_{4444})$ (2,5-PyrA)$]_{0.9}$ $[Li(2,5\text{-PyrA})]_{0.1}$	4.15	1.02	3.13

Table S4: Main interacting donor and acceptor NBOs and the second order perturbation energy E for the $(2\text{-PyrA})^-$ anion and its Li^+ ion-pair.

From	To	2-PyrA	Li^+–2-PyrA
Donor NBO	Acceptor NBO	E (kcal/mol)	
σ C1 – N1	π^* C4 – C5	42.75	199.20
π C2 – C3	σ^* C1 – N1	33.50	44.21
π C2 – C3	π^*C4 – C5	26.45	25.74
π C4 – C5	σ^*C1 – N1	21.50	22.73
π C4 – C5	π^*C2 –C3	29.34	179.32
LP O2	π^*Ca –O1	134.73	27.61
σ C1 – N1	π^*Ca –O1	48.80	34.21
π C4 – C5	σ^*C1 – N1	161.29	22.73
π C4 – C5	σ^*C2 –C3	218.62	28.88
LP O 1	π^*Ca – O2	23.25	99.84
LP O1	σ^*C1 – Ca	26.24	15.46
LP O2	σ^*C1 – Ca	22.65	
LP N1	σ^*C4 – C5	11.31	8.50
LP N1	σ^*C1 –C2	10.70	9.48
σ C1 – N1	π^*C2 –C3	19.69	133.03
σ C1 – N1	π^*Ca–O2		34.21
σ C1 – N1	π^*C4 –C5	42.75	35.24

Table S5: Main interacting donor and acceptor NBOs and the second order perturbation energy E for the $(3\text{-PyrA})^-$ anion and its Li^+ ion-pair.

From	To	3-PyrA	Li^+–3-PyrA
Donor NBO	Acceptor NBO	E kcal/mol	
σ C1 – N1	π*C4 – C5	38.10	
σ C 3 – C2	σ*C1 – N1	40.42	
σ C 3 – C2	π*C4 – C5	28.78	
π C4 – C5	σ*C1 –N1	22.84	
π C4 – C5	σ*C3– C2	27.78	
LP O1	π*C2 – Ca	22.86	18.41
LP O1	π*Ca – O2	142.82	18.89
LP O2	π*C2 – Ca	22.97	18.52
LP O2	π*Ca = O1	22.80	19.03
σ C1 – N1	σ*C3 – C2	124.99	
σ C4 – C3	π*Ca – O2	73.94	
σ C4 – C3	σ*C3 – C2	92.60	
LP N1	σ*C1– C2	9.70	
LP N1	σ*C1– H	4.61	
LP N1	σ*C1– C5	10.40	
LP N1	σ*C5– H	5.14	
σ C 5– N1	σ*C1 – C2		210.51
σ C3– N1	σ*C3 – C4		242.33
π C1– C2	σ*C5 – N1		24.35
π C1– C2	σ*C3 – C4		33.66
σ C3– C4	σ*C1– C2		23.89
σC3– C4	σ*C5– N1		40.90

Table S6: Main interacting donor and acceptor NBOs and the second order perturbation energy E for the $(4\text{-PyrA})^-$ anion and its Li^+ ion-pair.

From	To	4-PyrA	Li^+–4-PyrA
Donor NBO	Acceptor NBO	E kcal/mol	
π C 1 – C2	σ*C4 – C3	29.99	32.27
π C 1 – C2	σ*C5 – N1	27.04	28.31
σ C4 – C3	π*C1 – C2	26.05	25.51
σ C4 – C3	σ*C5 – N1	45.80	36.67
σ C5 – N1	π*C 1 – C2	33.25	34.96
LP O2	σ*C3 – Ca	23.22	0.99
LP O2	σ*Ca – O1	22.57	18.95
LP O2	LP*Ca	244.22	206.27
LP O1	σ*C3 – Ca	23.22	18.79
LP O1	π*Ca – O2	22.57	18.96
π C 1 – C2	σ*C4 – C3	168.46	3.25
σ C5 – N1	π*C1 – C2	145.58	217.56
σ C5 – N 1	σ*C 4 – C3	90.27	256.64
LP N1	π*C1– C2	9.86	10.22
LP N1	σ*C1– H	4.98	5.15
LP N1	π*C4– C5	9.86	10.22
LP N1	σ*C5– H	4.98	5.15

Table S7: Main interacting donor and acceptor NBOs and the second order perturbation energy E for the $(2,5\text{-PyrA})^-$ anion and its Li^+ ion-pair.

From	To	2,5-PyrA	Li^+–2,5-PyrA
Donor NBO	Acceptor NBO	E kcal/mol	
σ C1 – N1	σ^* C 2 – N2	25.55	19.85
σ C1 – N1	σ^* C3 – C4	37.33	31.59
σ C2 – N2	σ^*C1 – N1	22.42	28.30
σ C2 – N2	π^*C3 – C4	33.10	34.08
σ C3 – C4	σ^* C1 – N1	24.15	27.60
σ C3 – C 4	σ^* C2 – N2	26.38	26.37
LP O2	σ^*C1 – Ca	23.08	26.34
LP O2	σ^*Ca– O1	136.53	27.69
LP O1	σ^*C1 – Ca	26.78	15.92
LP O1	σ^*Ca – O2	23.23	99.57
σ C1 – N1	σ^*Ca – O1	44.14	30.33
σ C2 – N2	σ^*C1 – N1	225.77	218.96
π C3 – C4	σ^*C1 – N1	155.98	174.89