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ILs through the looking glass: Electrostatics and structure probed using *charge-inverted* ionic liquid pairs

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Contents

Syntheses of compounds C_nC_1CpH (1a,b) and $K[C_nC_1Cp]$ (2a,b)

1-*n*-butyl-3-methylcyclopentadiene (1a) (C_4C_1CpH): The preparation was according to the general procedure presented in the article using 1.93 g (20 mmol) of 3-methylcyclopent-2-enone and 30 mL (30 mmol) of a 1 M solution of *n*-BuMgBr in diethyl ether. 2.9 mL of glacial acetic acid in 9 mL of water was used for the hydrolysis and 2.5 g of a saturated solution of Na_2CO_3 in water for the neutralization. The crude orange-red oil was distilled trap-to-trap at 100 °C, yielding 0.43 g (16 %) of a pale-yellow liquid, corresponding to a mixture of isomers of **1a**.

1-*n*-hexyl-3-methylcyclopentadiene (1b) (C_6C_1CpH): The preparation was according to the general procedure presented in the article using 1.93 g (20 mmol) of 3-methylcyclopent-2-enone and 30 mL (30 mmol) of a 1 M solution of *n*-HexMgBr in diethyl ether. 2.9 mL of glacial acetic acid in 9 mL of water was used for the hydrolysis and 2.5 g of a saturated solution of Na_2CO_3 in water for the neutralization. The crude orange-red oil was distilled trap-to-trap at 120 °C, yielding 1.37 g (49 %) of a pale-yellow liquid, corresponding to a mixture of isomers of **1b**.

1-*n*-butyl-3-methylcyclopentadienyl potassium (2a) ($K[C_4C_1Cp]$): The preparation was according to the general procedure presented in the article using 1.13 g (8.4 mmol) of **1a** and 0.40 g (10.8 mmol) of KH, yielding 0.53 g of an off-white deliquescent and pyrophoric powder. Yield: 36%.
^{1}H NMR (300 MHz, C_5D_5N): δ 5.96 (s, 1H, H_{Cp}), 5.93 (s, 1H, H_{Cp}), 5.90 (s, 1H, H_{Cp}), 2.85 (t, 2H, C_1CH_2, $^3J_{HH}$=6 Hz), 2.56 (s, 3H, CH_3), 1.82 (q, 2H, C_2CH_2, $^3J_{HH}$=6 Hz), 1.49 (dt, 2H, C_3CH_2, $^3J_{HH}$=6 Hz), 0.96 (t, 3H, C_4CH_3, $^3J_{HH}$=6 Hz). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_5D_5N): δ 121.1 ($C1_{Cp}$ or $C3_{Cp}$), 113.7 ($C1_{Cp}$ or $C3_{Cp}$), 105.2 ($C4_{Cp}$ or $C5_{Cp}$), 104.3 ($C4_{Cp}$ or $C5_{Cp}$), 103.3 ($C2_{Cp}$), 36.7 (C_2CH_2), 32.0 (C_1CH_2), 24.4 (C_3CH_2), 16.9 (CH_3), 15.0 (C_4CH_2).

1-*n*-hexyl-3-methylcyclopentadienyl potassium (2b) ($K[C_6C_1Cp]$): The preparation was according to the general procedure presented in the article using 1.37 g (9.78 mmol) of **1b** and 0.47 g (11.7 mmol) of KH, yielding 0.96 g of a pale-orange deliquescent and pyrophoric powder. Yield: 49%.

^{1}H NMR (300 MHz, C_5D_5N): δ 5.80 (s, 1H, H_{Cp}), 5.76 (br, 2H, H_{Cp}), 2.76 (t, 2H, C_1CH_2, $^3J_{HH}$=6 Hz), 2.45 (s, 3H, CH_3), 1.78 (q, 2H, C_2CH_2, $^3J_{HH}$=6 Hz), 1.53-1.27 (br, 2H, C_3-C_5CH_2), 0.92 (t, 3H, C_6CH_3, $^3J_{HH}$=6 Hz). ^{13}C{^{1}H} NMR (75.43 MHz, C_5D_5N): 121.3 ($C1_{Cp}$ or $C3_{Cp}$), 113.8 ($C1_{Cp}$ or $C3_{Cp}$), 105.4 ($C4_{Cp}$ or $C5_{Cp}$), 104.1 ($C4_{Cp}$ or $C5_{Cp}$), 103.1 ($C2_{Cp}$), 34.2 (C_2CH_2), 32.9 ($C_{3\text{-}5}CH_2$), 32.1 (C_1CH_2), 31.1 ($C_{3\text{-}5}CH_2$), 23.6 ($C_{3\text{-}5}CH_2$), 16.5 (CH_3), 14.8 (C_6CH_3).

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of $K[C_nC_1Cp]$

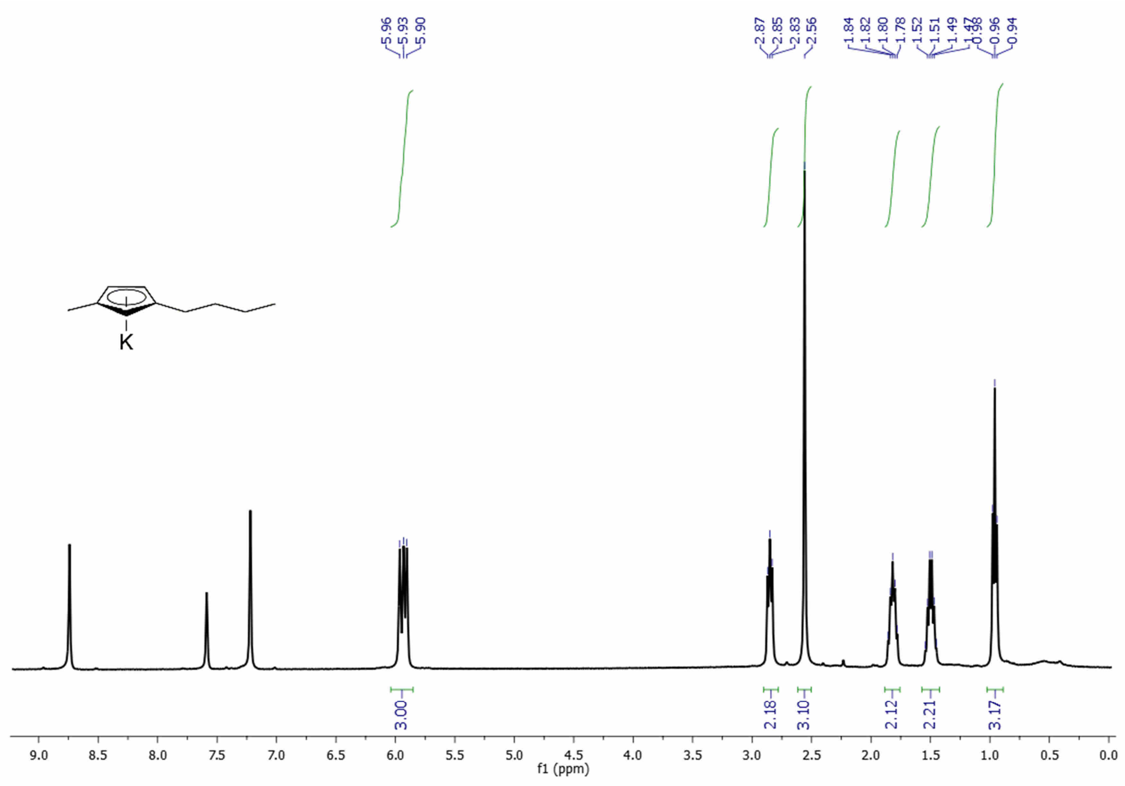

Figure S1 ^{1}H NMR (300 MHz) spectrum of **2a** ($K[C_4C_1Cp]$) in C_5D_5N.

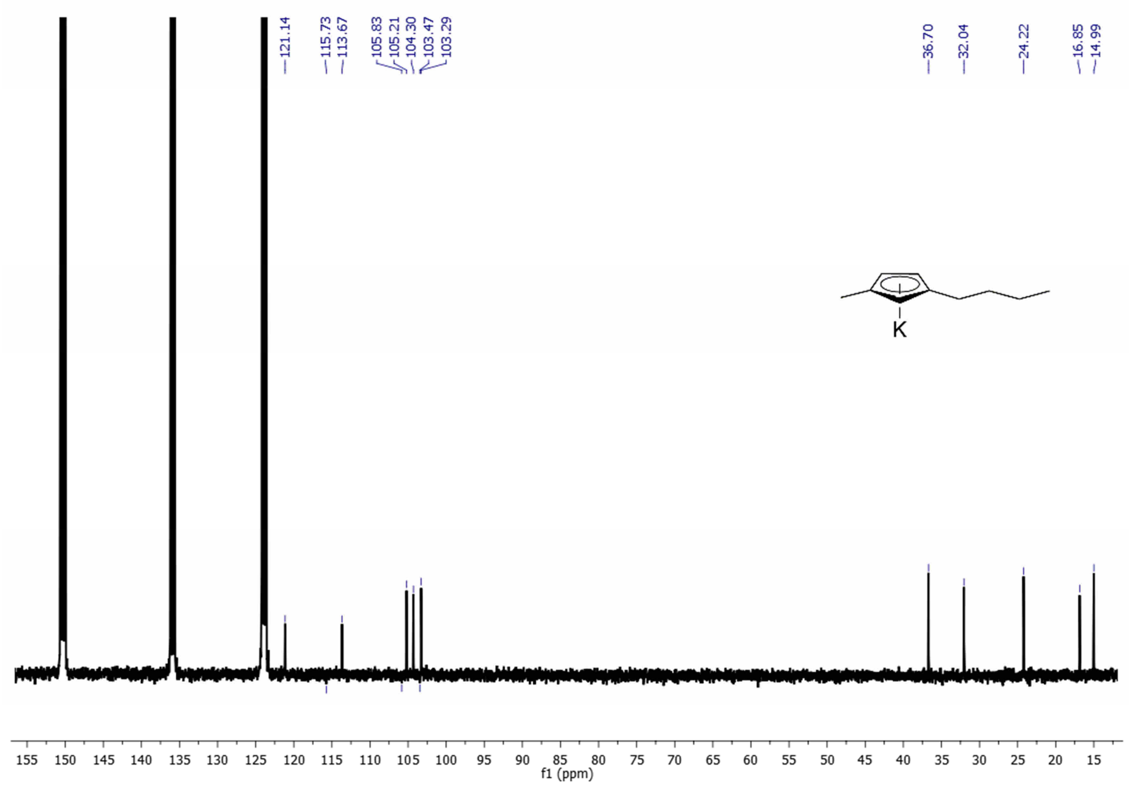

Figure S2 $^{13}C\{^{1}H\}$ NMR (75.43 MHz) spectrum of **2a** ($K[C_4C_1Cp]$) in C_5D_5N.

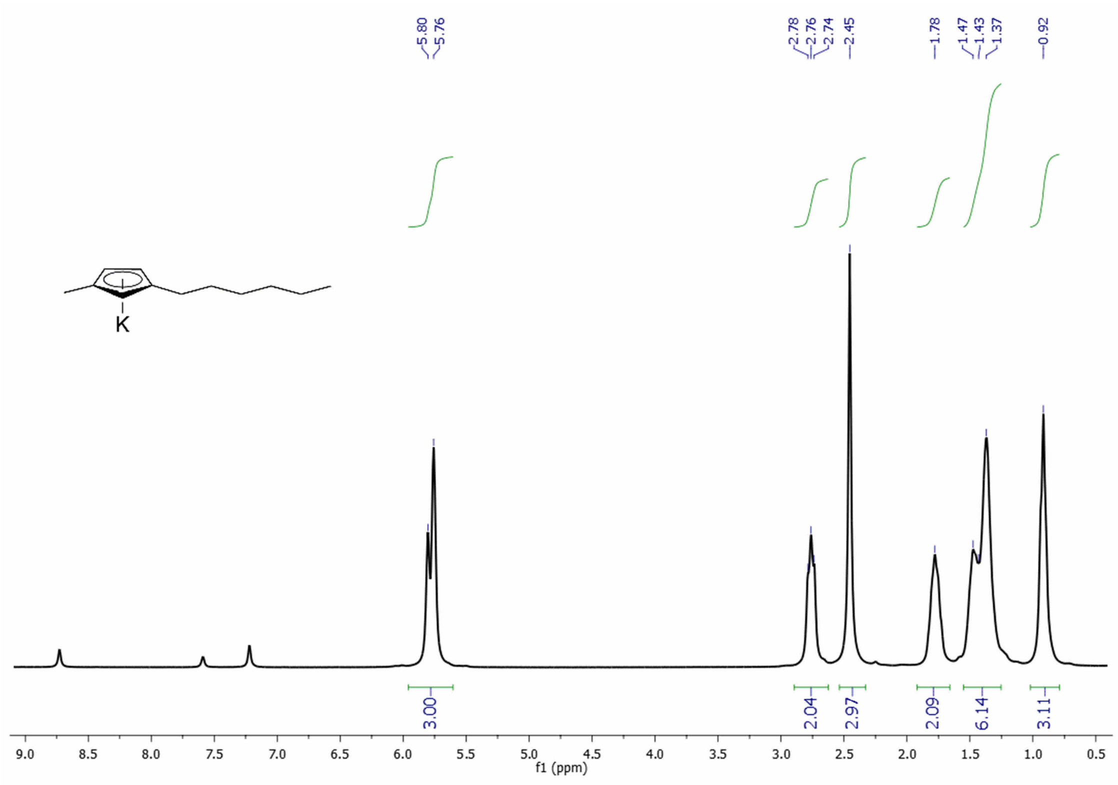

Figure S3 ^{1}H NMR (300 MHz) spectrum of **2b** (K[C_6C_1Cp]) in C_5D_5N.

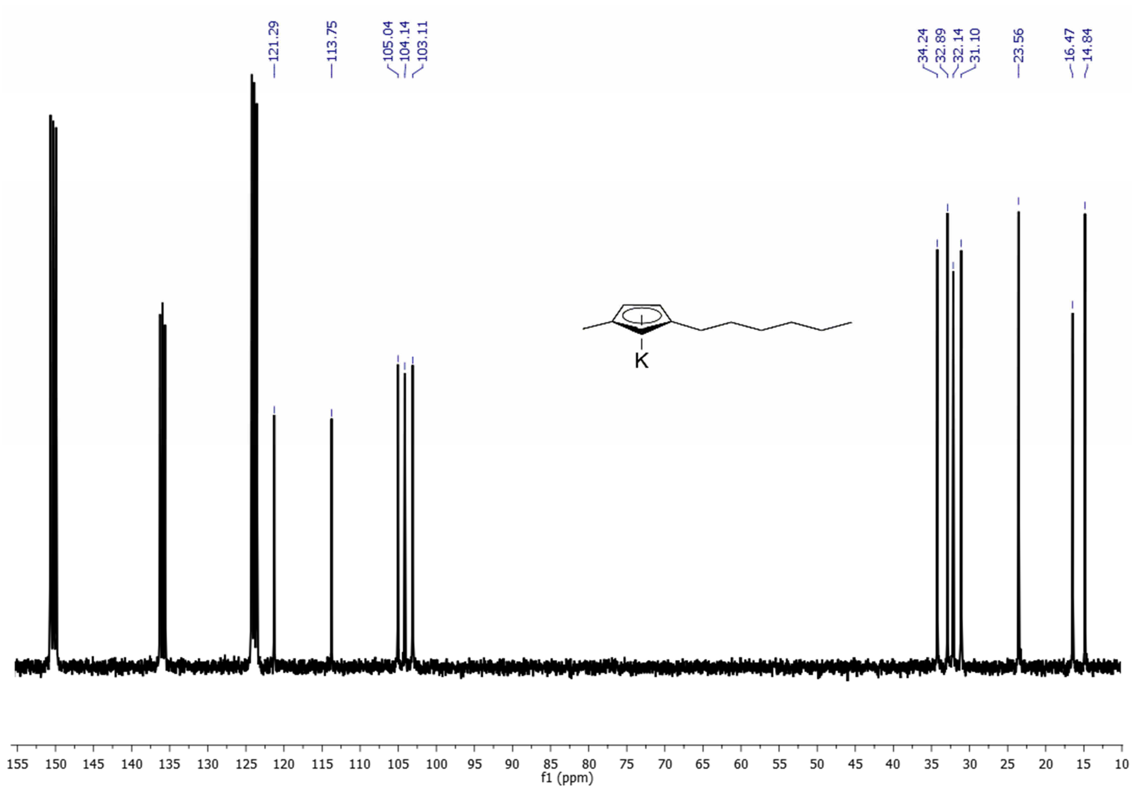

Figure S4 ^{13}C{^{1}H} NMR (75.43 MHz) spectrum of **2b** (K[C_6C_1Cp]) in C_5D_5N.

Table S1 Ionic polarizabilities, α, and radii, *r*, of alkali halides (data from Y. Marcus, *Ionic Liquids Properties*, Springer, Berlin, 2016). T_m and T_{eb} correlations.

salt	α_{cat}	α_{an}	r_{cat}	r_{an}	T_m	$T_{m,cal}$	δ [a]	T_{eb}	$T_{eb,cal}$	δ [a]
	10^{-3} nm^3		pm		K		%	K		%
NaF	0.26	0.88	106	123	1266	1277	1	1977	1969	0
KF	1.07	0.88	140	123	1125	1132	1	1775	1767	0
RbF	1.63	0.88	152	123	1106	1080	-2	1683	1689	0
CsF	2.73	0.88	175	123	976	978	0	1524	1529	0
NaCl	0.26	3.42	106	170	1074	1081	1	1738	1748	1
KCl	1.07	3.42	140	170	1043	1027	-2	1680	1692	1
RbCl	1.63	3.42	152	170	995	1001	1	1663	1656	0
CsCl	2.73	3.42	175	170	915	942	3	1570	1570	0
NaBr	0.26	4.85	106	188	1020	1014	-1	1663	1666	0
KBr	1.07	4.85	140	188	1007	987	-2	1656	1652	0
RbBr	1.63	4.85	152	188	965	967	0	1613	1627	1
CsBr	2.73	4.85	175	188	909	920	1	1573	1559	-1
NaI	0.26	7.51	106	206	933	939	1	1577	1567	-1
KI	1.07	7.51	140	206	954	942	-1	1596	1600	0
RbI	1.63	7.51	152	206	920	929	1	1573	1587	1
CsI	2.73	7.51	175	206	899	892	-1	1553	1536	-1

[a] δ represents the relative deviations between the experimental and calculated temperatures.

$$T_{m,cal} = -(33.4\pm4.9)(\alpha_{an}/\alpha_{cat})^{0.5} + (225.4\pm9.2).10^{3}(r_{cat}+r_{an}) - (88\pm14)(r_{cat}/r_{an})^{2} + 419\pm30$$

$$T_{eb,cal} = -(55.9\pm3.6)(\alpha_{an}/\alpha_{cat})^{0.5} + (256.2\pm6.7).10^{3}(r_{cat}+r_{an}) - (196\pm10)(r_{cat}/r_{an})^{2} + 1098\pm21$$

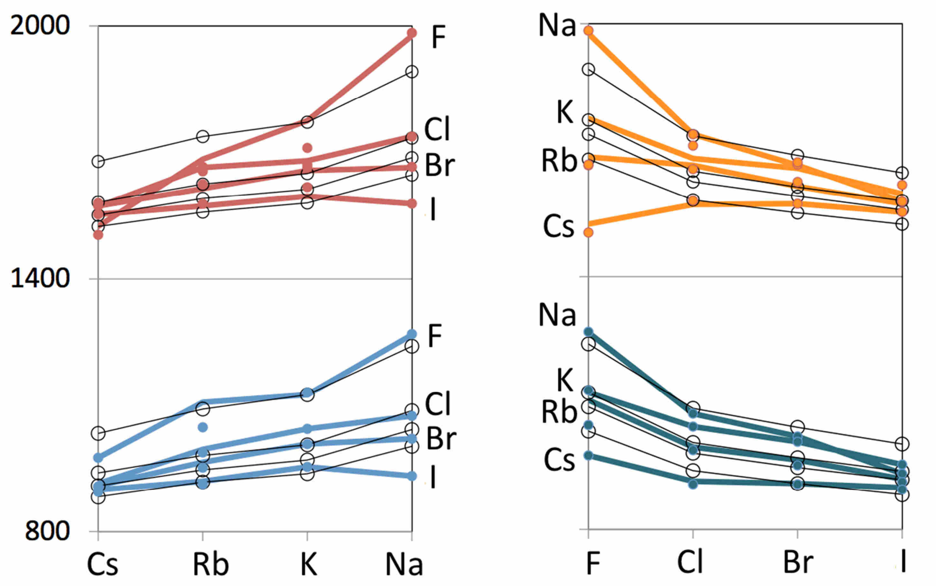

Figure S5 T_m and T_{eb} correlations based solely on ionic size.

$T_{m,cal} = (204 \pm 16).10^3\,(r_{cat}+r_{an}) + 344 \pm 53$; $T_{eb,cal} = (212 \pm 18).10^3\,(r_{cat}+r_{an}) + 967 \pm 57$.