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Electronic Supplementary Information

for

# Imidazolium-based ionic liquids with large weakly coordinating anions

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## Contents

1.	X-ray structure of [BMPYRR][BAr <sup>F</sup> ]	2
2.	DSC traces	3
3.	NMR spectra:	7
	• $[EMIM][BAr^{F}]$	7
	• $[EDMIM][BAr^{F}]$	9
	• [HMIM][BAr <sup>F</sup> ]	11
	• [EMBIM][BAr <sup>F</sup> ]	13
	• [IDiPPH][BAr <sup>F</sup> ]	15
	• $[BMPYRR][BAr^F]$	17
	• $[EMIM][Al(O^{t}C_{4}F_{9})_{4}]$	19
	• $[EDMIM][Al(O^{t}C_{4}F_{9})_{4}]$	21
	• $[HMIM][Al(O^{t}C_{4}F_{9})_{4}]$	23
	• $[\text{EMBIM}][\text{Al}(\text{O}^{t}\text{C}_{4}\text{F}_{9})_{4}]$	25

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#### X-ray structure of [BMPYRR][BAr<sup>F</sup>]



Figure S1: ORTEP representation of [BMPYRR][BAr<sup>F</sup>] showing one of two molecules in the asymmetric unit. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity. For the X-ray CIF data, see Table 1 of the main manuscript.

#### **DSC traces**



Figure S2: DSC trace for  $[EMIM][BAr^{F}]$ . Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S3: DSC trace for [EDMIM][BAr<sup>F</sup>]. Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S4: DSC trace for  $[HMIM][BAr^{F}]$ . Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S5: DSC trace for [EMBIM][BAr<sup>F</sup>]. Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S6: DSC trace for  $[EMIM][Al(O^{t}C_{4}F_{9})_{4}]$ . Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S7: DSC trace for [EDMIM][Al( $O^{t}C_{4}F_{9}$ )<sub>4</sub>]. Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S8: DSC trace for  $[HMIM][Al(O^{t}C_{4}F_{9})_{4}]$ . Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.



Figure S9: DSC trace for [EMBIM][Al( $O^{t}C_{4}F_{9}$ )<sub>4</sub>]. Key: blue = first heating cycle, green = cooling cycle, red = second heating cycle.

#### **Spectral Data**

#### [EMIM][BAr<sup>F</sup>]:



Figure S10:  $^{1}$ H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).



Figure S11: <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 298 K).



Figure S12: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_7_Figure_2.jpeg)

Figure S13:  ${}^{19}F{}^{1}H{}$  NMR spectrum (CDCl<sub>3</sub>, 298 K).

[EDMIM][BAr<sup>F</sup>]:

![](_page_8_Figure_1.jpeg)

Figure S14: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_8_Figure_3.jpeg)

Figure S15: <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_9_Figure_0.jpeg)

Figure S16: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_9_Figure_2.jpeg)

Figure S17:  ${}^{19}F{}^{1}H{}$  NMR spectrum (CDCl<sub>3</sub>, 295 K).

[HMIM][BAr<sup>F</sup>]:

![](_page_10_Figure_1.jpeg)

Figure S18: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_10_Figure_3.jpeg)

Figure S19:  $^{13}C{^{1}H}$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_11_Figure_0.jpeg)

Figure S20:  ${}^{19}F{}^{1}H$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

[EMBIM][BAr<sup>F</sup>]:

![](_page_12_Figure_1.jpeg)

Figure S21: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_12_Figure_3.jpeg)

Figure S22: <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

![](_page_13_Figure_0.jpeg)

Figure S23:  $^{13}C{^{1}H}$  NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

[IDiPPH][BAr<sup>F</sup>]:

![](_page_14_Figure_1.jpeg)

Figure S24: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_14_Figure_3.jpeg)

Figure S25: <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_15_Figure_0.jpeg)

Figure S26: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 298 K).

### [BMPYRR][BAr<sup>F</sup>]:

![](_page_16_Figure_1.jpeg)

Figure S27: <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_16_Figure_3.jpeg)

Figure S28: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_17_Figure_0.jpeg)

Figure S29: DEPT-135 NMR spectrum (CDCl<sub>3</sub>, 298 K).

![](_page_17_Figure_2.jpeg)

Figure S30:  $^{19}F{}^{1}H$  NMR spectrum (CDCl<sub>3</sub>, 298 K).

#### [EMIM][Al(O<sup>t</sup>C<sub>4</sub>F<sub>9</sub>)<sub>4</sub>]:

![](_page_18_Figure_1.jpeg)

Figure S31: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_18_Figure_3.jpeg)

Figure S32: <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

![](_page_19_Figure_0.jpeg)

Figure S33: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

![](_page_19_Figure_2.jpeg)

Figure S34:  ${}^{19}F{}^{1}H$  NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

#### [EDMIM][Al(O<sup>t</sup>C<sub>4</sub>F<sub>9</sub>)<sub>4</sub>]:

![](_page_20_Figure_1.jpeg)

Figure S35: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_20_Figure_3.jpeg)

Figure S36: <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

![](_page_21_Figure_0.jpeg)

Figure S37: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

![](_page_21_Figure_2.jpeg)

Figure S38:  ${}^{19}F{}^{1}H{}$  NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

[HMIM][Al(O<sup>t</sup>C<sub>4</sub>F<sub>9</sub>)<sub>4</sub>]:

![](_page_22_Figure_1.jpeg)

Figure S39: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_22_Figure_3.jpeg)

Figure S40:  $^{13}C{^{1}H}$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_23_Figure_0.jpeg)

Figure S41:  ${}^{19}F{}^{1}H$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

#### [EMBIM][Al(O<sup>t</sup>C<sub>4</sub>F<sub>9</sub>)<sub>4</sub>]:

![](_page_24_Figure_1.jpeg)

Figure S42: <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

![](_page_24_Figure_3.jpeg)

Figure S43: <sup>1</sup>H NMR spectrum (( $CD_3$ )<sub>2</sub>CO, 298 K).

![](_page_25_Figure_0.jpeg)

Figure S44:  ${}^{13}C{}^{1}H$  NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).

![](_page_25_Figure_2.jpeg)

Figure S45: <sup>19</sup>F{<sup>1</sup>H} NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>CO, 298 K).