Electronic Supplementary Information

(ESI)

Identifying the Suitable Ionic Liquid Electrolytes in Al Dual-Ion Batteries: Role of Electrochemical Window, Conductivity and Voltage

Surya Sekhar Manna,[†] Preeti Bhauriyal,[†] Biswarup Pathak,[†,*]

†Discipline of Chemistry, Indian Institute of Technology (IIT) Indore, Indore, Madhya Pradesh 453552, India
Email: biswarup@iiti.ac.in

Contents:

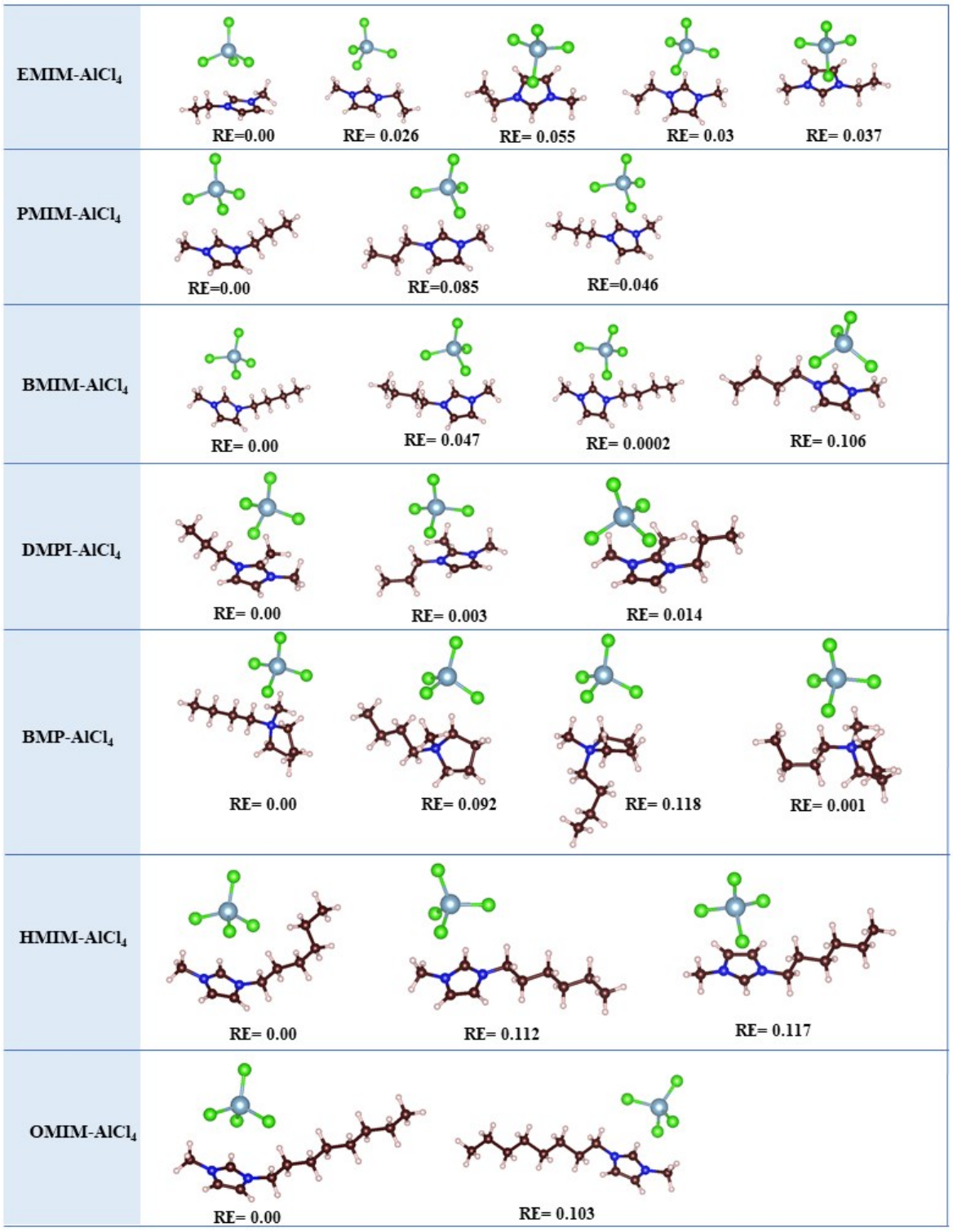

Figure S1. Different orientation of considered ionic liquid. RE (in eV) is the relative energy.

Table S1. Cathodic and anodic potential value (vs. Al/Al^{3+}).

Electrolyte	Cathodic limiting potential (V_{CL})	Anodic limiting potential (V_{AL})
EMIM-$AlCl_4$	-2.0	2.34[1]
PMIM- $AlCl_4$	-2.2	2.5[2]
BMIM- $AlCl_4$	-2.1	2.6[3]
DMPI- $AlCl_4$	-1.4	2.23[4]
BMP- $AlCl_4$	-0.1	0.15[5]
Urea- $AlCl_4$	-1.4	1.7[6]
AcAm-$AlCl_4$	-1.25	0.85[7]

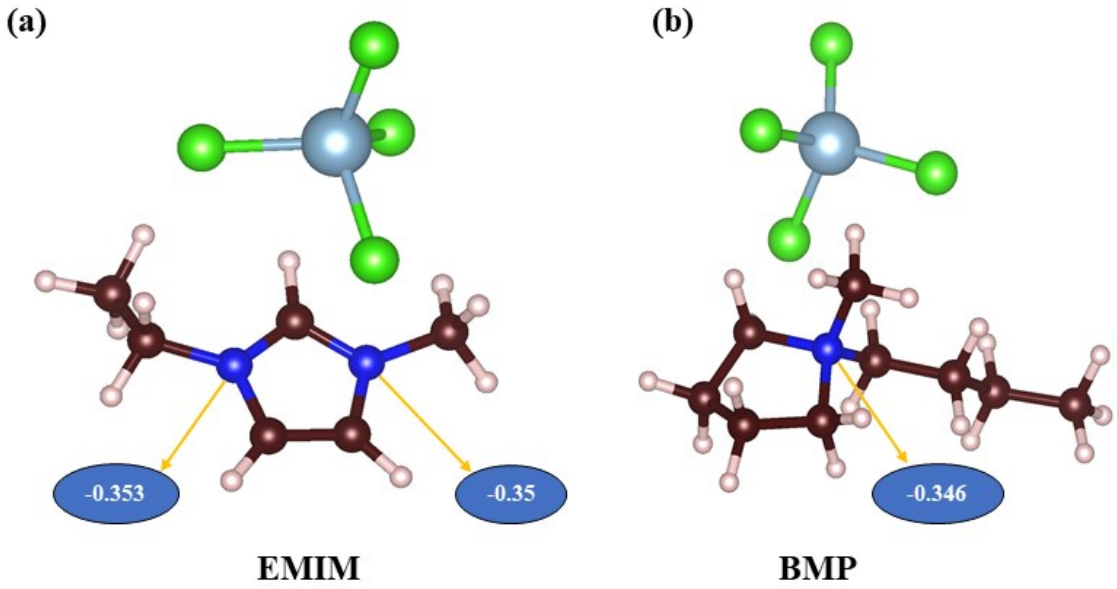

Figure S2. NBO charges on nitrogen atoms of (a) EMIM-$AlCl_4$ and (b) BMP-$AlCl_4$.

Table S2. Viscosity and density of the considered ionic liquid electrolytes at room temperature.

Ionic Liquid	Viscosity (P)	Density (kg/m^3)
EMIM-$AlCl_4$	0.18	1294[8]
PMIM-$AlCl_4$	0.19	1262[9]
BMIM-$AlCl_4$	0.24	1238[10]
DMPI-$AlCl_4$	0.32	1170[11]
HMIM-$AlCl_4$	0.40	1195[12]
OMIM-$AlCl_4$	0.42	1193[12]
Urea-$AlCl_4$	0.25	1500[13]
AcAm-$AlCl_4$	0.59	1450[13]

Table S3. Cationic radii of the considered ionic liquid electrolytes. The anion ($AlCl_4^-$) radii is 2.84 Å.

Cation (R_+)	vdW volume ($Å^3$)	Radii (Å)
EMIM	115.53	3.02
PMIM	132.53	3.16
BMIM	149.49	3.29
DMPI	149.43	3.29
HMIM	183.42	3.52
OMIM	217.33	3.73
Urea	154.21	3.32
AcAm	165.83	3.4

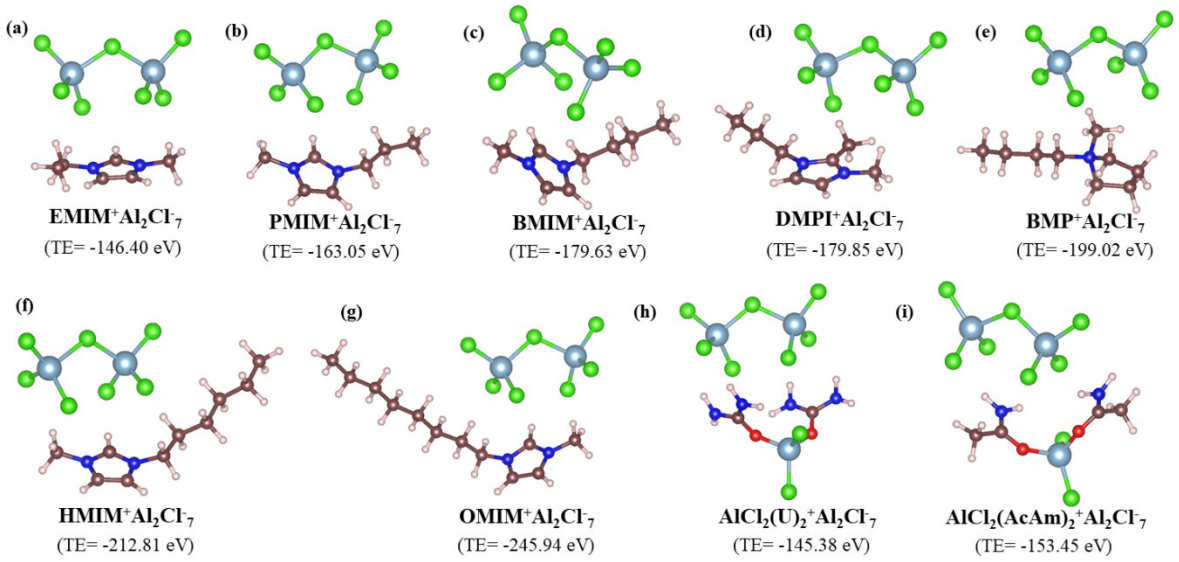

Figure S3. Optimised structure and corresponding total energy (TE) of Cation$^{+}Al_2Cl_7^{-}$ systems, (a) $EMIM^{+}Al_2Cl_7^{-}$, (b) $PMIM^{+}Al_2Cl_7^{-}$, (c) $BMIM^{+}Al_2Cl_7^{-}$, (d) $DMPI^{+}Al_2Cl_7^{-}$, (e) $BMP^{+}Al_2Cl_7^{-}$, (f) $HMIM^{+}Al_2Cl_7^{-}$, (g) $OMIM^{+}Al_2Cl_7^{-}$, (h) $AlCl_2(U)_2^{+}Al_2Cl_7^{-}$, (i) $AlCl_2(AcAm)_2^{+}Al_2Cl_7^{-}$

References

1. H. Sun, W. Wang, Z. Yu, Y. Yuan, S. Wang and S. Jiao, *Chem. Commun.*, 2015, **51**, 11892-11895.

2. G. E. Gray, J. Winnick and P. A. Kohl, *J. Electrochem. Soc.,* 1996, **143**, 3820.

3. H. Wang, S. Gu, Y. Bai, S. Chen, N. Zhu, C. Wu and F. Wu, *J. Mater. Chem. A*, 2015, **3**, 22677–22686.

4. Z. Lv, M. Han, J. Sun, L. Hou, H. Chen, Y. Li and M. -C. Lin, *Journal of Power Sources*, 2019, **418**, 233–240.

5. P. Giridhar, S. Zein El Abedin and F. Endres, *Electrochimica Acta*, 2012, **70**, 210– 214.

6. M. Angell, C. -J. Pan, Y. Rong, C. Yuan, M. -C. Lin, B. -J. Hwang and H. Dai, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 834–839.

7. M. Li, B. Gao, C. Liu, W. Chen, Z. Shi, X. Hu and Z. Wang, *Electrochimica Acta*, 2015, **180**, 811–814.

8. S. V. Sambasivarao and O. Acevedo, *J. Chem. Theory Comput.*, 2009, **5**, 1038–1050.

9. A. A. Jr. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, *The Journal of Physical Chemistry,* 1984, ***88***, 2614-2621.

10. Y. Zheng, K. Dong, Q. Wang, J. Zhang and X. Lu, *J. Chem. Eng. Data*, 2013, **58**, 32−42.

11. C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, *J. Chem. Eng. Data*, 2004, **49**, 954-964.

12. E. Gómez, B. González, A. Domínguez, E. Tojo and J. Tojo, *J. Chem. Eng. Data,* 2006, **51***,* 696-701.

13. C. Liu, W. Chen, Z. Wu, B. Gao, X. Hu, Z. Shi and Z. Wang, *Journal of Molecular Liquids* 2017, **247**, 57-63.