Ionic Liquids and their Modification with Diamondoids

Seminar talk presented by
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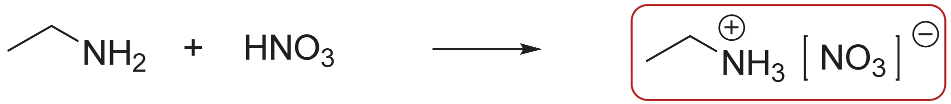
Ionic Liquids (IL)

- composition of purely anions and cations
- salts with melting points at or below 100 °C
- low volatility
- moisture- and air-stable
- consistent conductivity
- large liquid range
- tunable polarity
- nonflammability
- wide solubility
- high stability

B. Wang, L. Qin, T. Mu, Z. Xue, G. Gao, *Chem. Rev.* **2017**, *117*, 7113-7131.

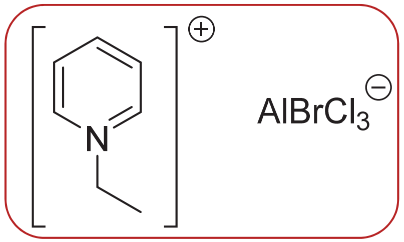
First generation



Walden, **1914**

similar physical properties to water
(clear, colorless, odorless liquid)

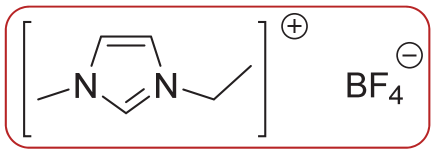
Second generation



Hurley and Wier, **1954**

are not stable in the presence of moisture
their acidity/basicity is not easy to regulate

Third generation



m.p. 15 °C

Wilkes and Zaworotko, **1992**

moisture- and air-stable,
may be dried conveniently in a vacuum oven at 80 °C

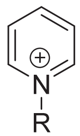
P. Walden, *Bull. Acad. Imp. Sci.* **1914**, *8* (6), 405–422,
F. H. Hurley, T. P. WIer, *J. Electrochem. Soc.* **1951**, *98*, 207-212,
J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1992**, 965-967.

Commonly used Cations and Anions for IL

C a t i o n s

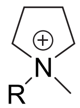
1-alkyl-3-methylimidazolium

$[C_nC_1im]^+$



1-alkylpyridinium

$[C_npyr]^+$



1-alkyl-1-methylpyrrolidinium

$[C_nC_1pyrr]^+$

$R_4N^{\oplus}$

tetraalkylammonium

$[C_4N]^+$

$R_4P^{\oplus}$

tetraalkylphosphonium

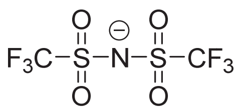
$[C_4P]^+$

$R_3S^{\oplus}$

trialkylsulfonium

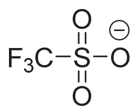
$[C_3S]^+$

A n i o n s



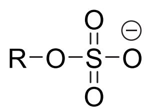
bis(trifluoromethylsulfonyl)imide

$[NTf_2]^-$



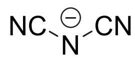
trifluoromethanesulfonate

triflate, $[OTf]^-$



alkylsulfate

$[C_nSO_4]^-$



dicyanamide

$[N(CN)_2]^-$

$^{\ominus}PF_6$

hexafluorophosphate

$[PF_6]^-$

$^{\ominus}BF_4$

tetrafluoroborate

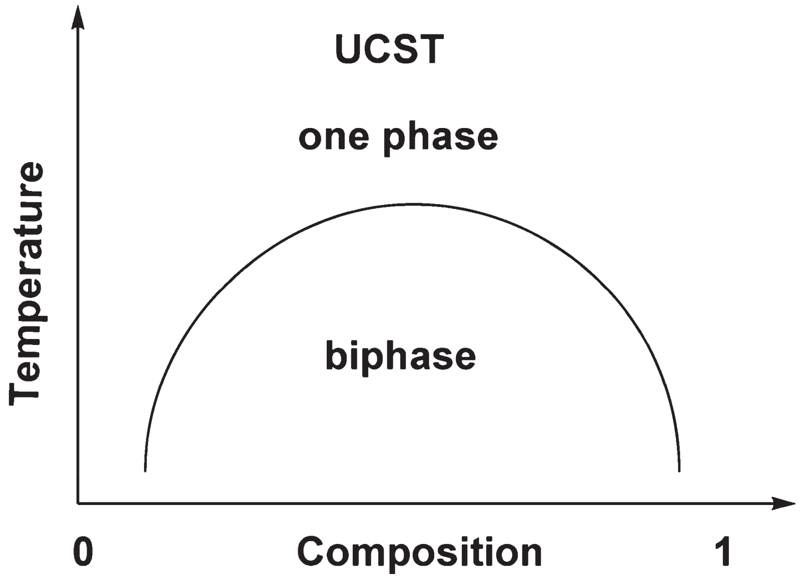
$[BF_4]^-$

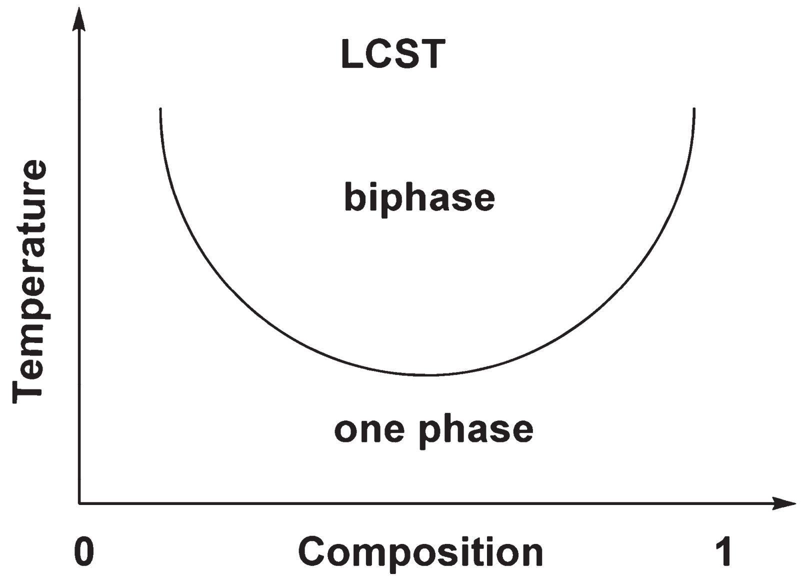
J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508-3576.

IL Applications

- alternative solvents
- electrolytes
- catalysts
- gas adsorbents
- lubricants
- extractants
- ionic liquid crystals
- explosives and propellant fuels

M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, *Chem. Rev.* **2017**, *117*, 7190-7239

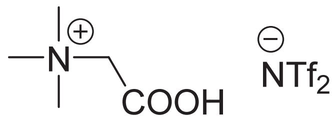




UCST = upper critical solution temperature   LCST = lower critical solution temperature

Applied in extraction and separation

Commonly used systems
with H_2O, alcohols, hydrocarbons

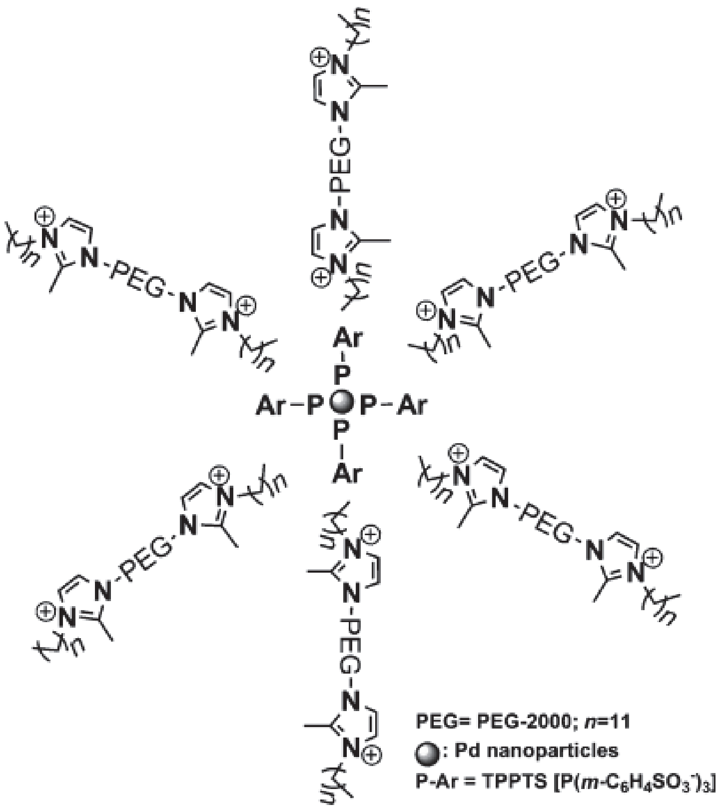


[Hbet][NTf_2]

- Selectively dissolve large quantities of rare earth metal oxides
- used as a draw solute in forward osmosis from high−salinity water (≤3.0 M)

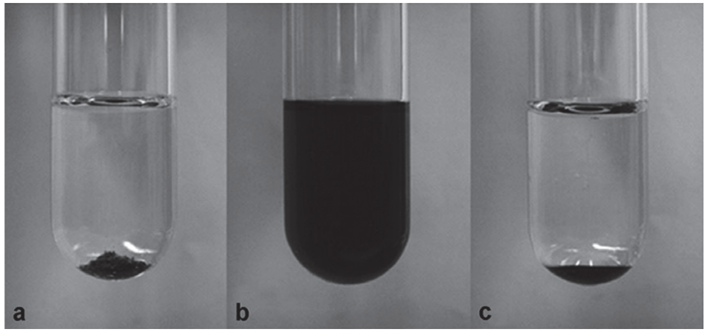
Y. Qiao, W. Ma, N. Theyssen, C. Chen, Z. Hou *Chem. Rev.* **2017**, *117*, 6881-6928,
N. Schaeffer, S. Grimes, C. Cheeseman *Inorg. Chim. Acta* **2016**, *439*, 55−60.

Thermoregulated phase separation of metal nanoparticles immobilized in PEG-functionalized IL



The thermomorphic IL ([PEG-2000-C_{12}MIM]$_{1.5}$ [tppt])-stabilized/modified palladium nanoparticles

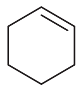
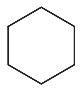
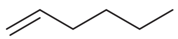
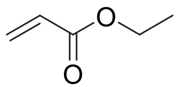
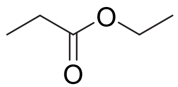
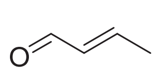
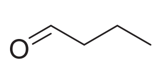
higher selectivity for the hydrogenation of the C=C bonds than commercially available (Pd/C and Rh/C)



a) catalyst, EtOAc, and substrate at 0 °C

b) reaction at 45 °C

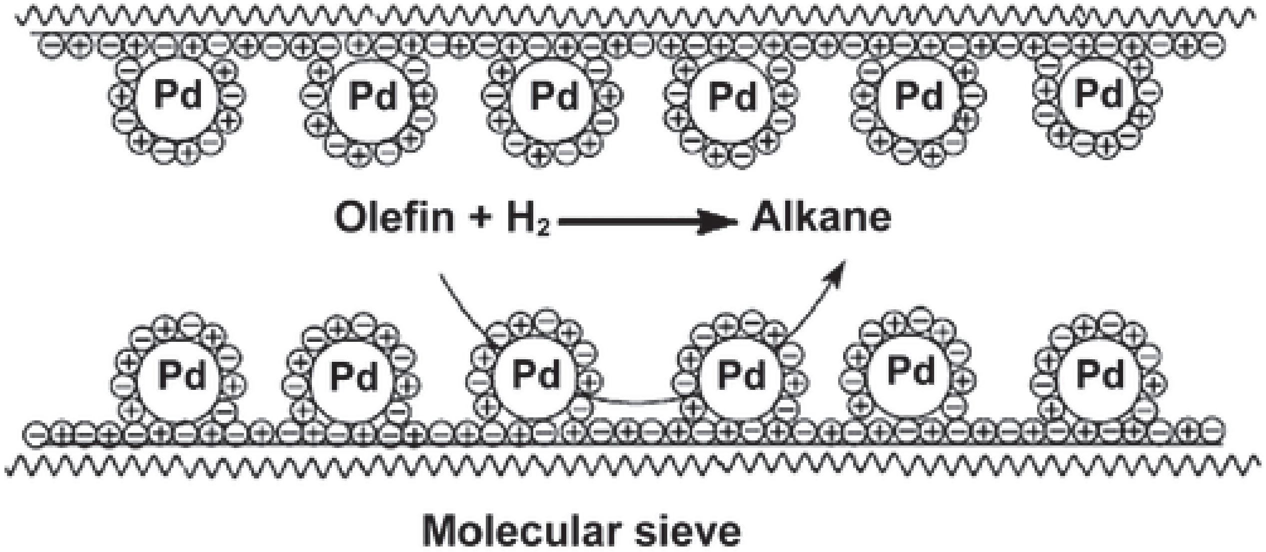
c) complete phase-separation after cooling to 0 °C

Substrate	Product	t , h	Conv., %	Yield, %
		4	100	100
		5	100	100
		2.5	100	100
		6	100	100

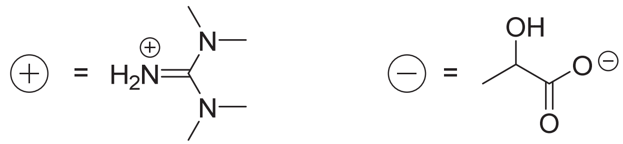
substrate/Pd = 1000, 45 °C, H_2 at atm. pressure

W. Zhu, Y. Yu, H. Yang, L. Hua, Y. Qiao, X. Zhao, Z. Hou *Chem. Eur. J.* **2013**, *19*, 2059.

Immobilization of Pd nanoparticles on the surface of a molecular sieve
by 1,1,3,3-tetramethylguanidinium lactate (TMGL)

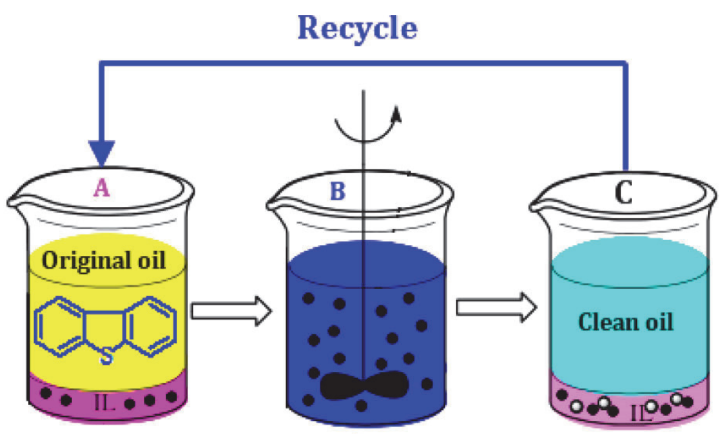


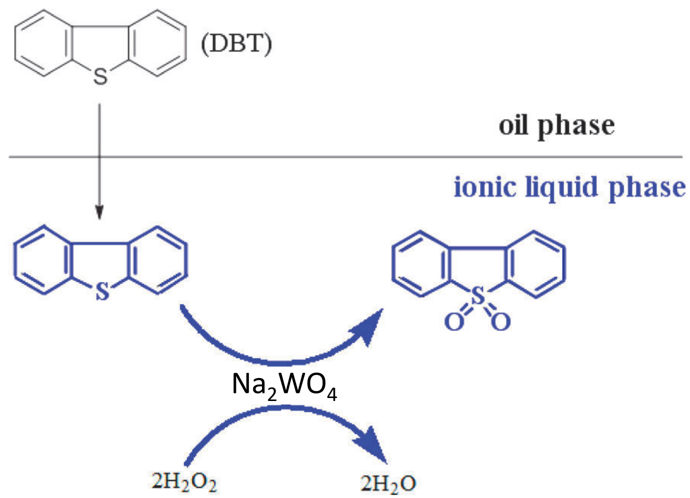
Various metals Au, Pt, Pd
were supported on SiO_2,
Al_2O_3,
TiO_2,
carbon nanotubes



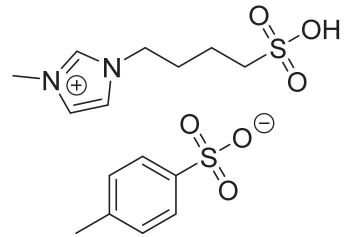
J. Huang, T. Jiang, H. Gao, B. Han, Z. Liu, W. Wu, Y. Chang, G. Zhao *Angew. Chem. Int. Ed.* **2004**, *43*, 1397-1399.

Oxidative Desulfurization





The sulfur content reduced from 500 to 3 $\mu g \cdot g^{-1}$ at 50 °C
removal ratio 99.4%

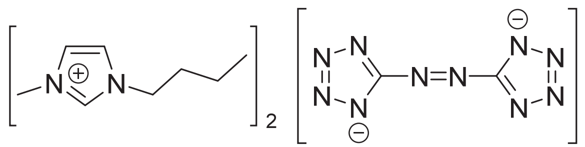


IL = $[(CH_2)_4SO_3HMIm][Tos]$

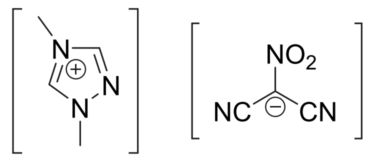
- Oxidation Of Alcohols
- Epoxidation of Alkenes
- Baeyer−Villiger Oxidation
- Oxidation of Alkanes

Catalysts based on V, Mo, Fe, Ce, Cu, Nb have been reported

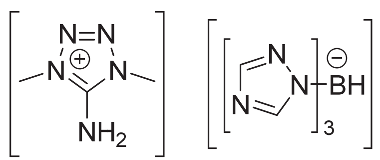
D. Liu, J. Gui, J. Ding, J. Ma, J. Lee, Z. Sun *React. Kinet., Mech. Catal.* **2011**, *104*, 111–123,
C. Dai, J. Zhang, C. Huang, Z. Lei *Chem. Rev.* **2017**, *117*, 6929-6983.



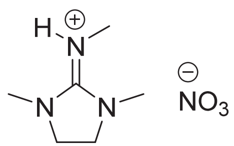
Imidazolium-Based Im-2
m.p. 3 °C



Triazolium-Based Tri-45
m.p. 61 °C



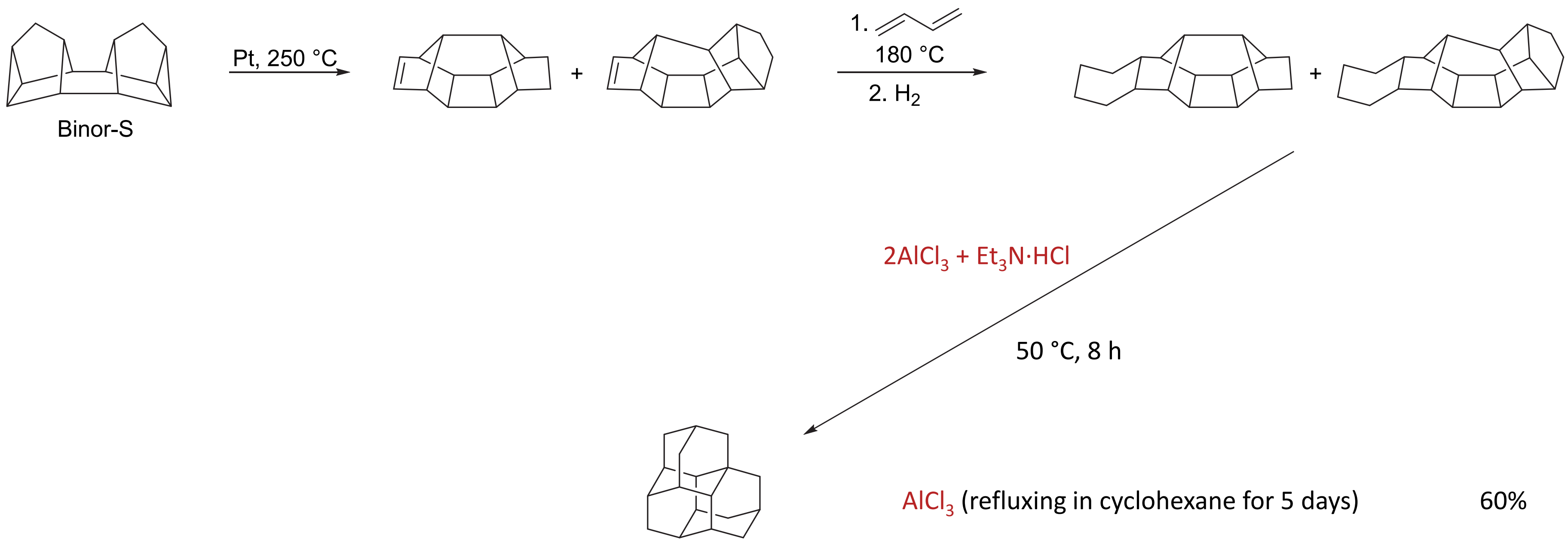
Tetrazolium-Based Tetra-7
m.p. 11.8 °C



Quaternary Ammonium-Based AM-10
m.p. 3 °C

Q. Zhang, J. n. M. Shreeve, *Chem. Rev.* **2014**, *114*, 10527-10574.

Application of IL in Triamanatane Synthesis



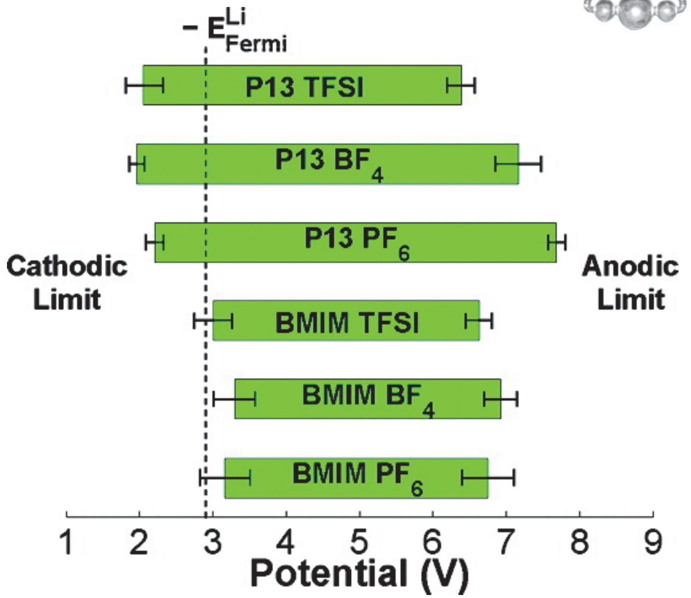
80%

$AlCl_3$ (refluxing in cyclohexane for 5 days)	60%
$B(OSO_2CF_3)_3$ (0 °C, Freon-113, 74 h)	70%
$CF_3SO_3H\text{-}SbF_5$ (0 °C, Freon-113, 74 h)	71%
$CF_3SO_3H\text{-}B(OSO_2CF_3)_3$ (0 °C, Freon-113, 74 h)	69%

R. I. Khusnutdinov, R. R. Mukminov, R. I. Aminov, L. M. Khalilov, E. S. Mescheryakova, U. M. Dzhemilev, *Tetrahedron Lett.* **2015**, *56*, 536-538.

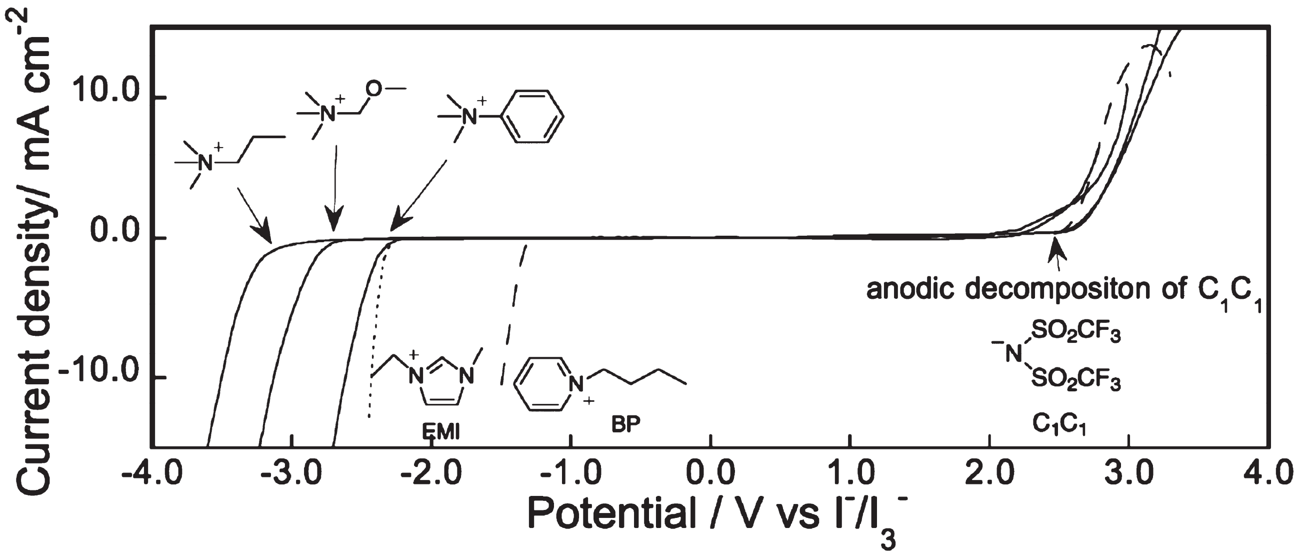
Electrolytes in Li/Na, Li-S_8, Li-O_2 Batteries

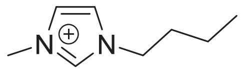
R_4N^+ or R_4P^+ as cations (stable towards reduction),
BF_4^-, PF_6^-, NTf_2^- as anions (stable towards oxidation)



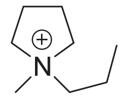
Electrochemical windows of Ils from MD and DFT calculations

Linear sweep voltammograms of [TFSA]-based ILs





1-butyl-3-methylimidazolium (BMIM)



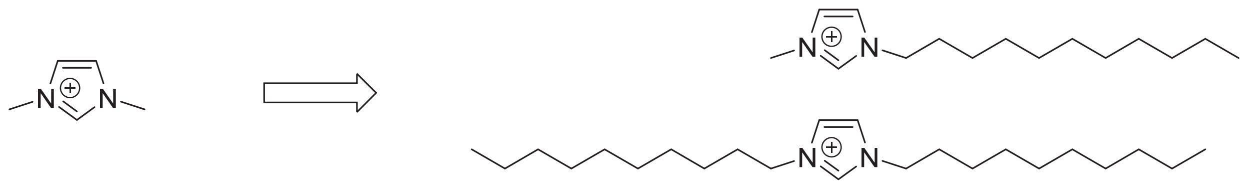
N,N-propylmethylpyrrolidinium (P13)

TFSI = $^-NTf_2$

M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, *Chem. Rev.* **2017**, *117*, 7190-7239,
S. P. Ong, O. Andreussi, Y. Wu, N. Marzari, G. Ceder, *Chem. Mater.* **2011**, *23*, 2979-2986.

Diamondoid IL

- cation decomposition under cathodic potentials is a major challenge

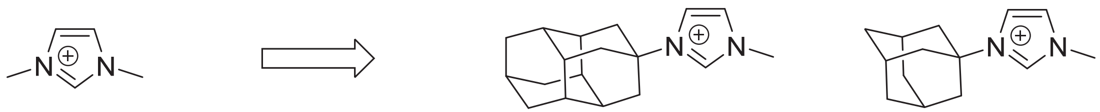


+

- does enhance stability

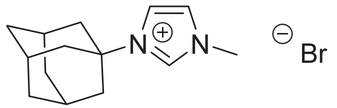
–

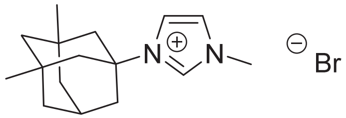
- major decreases in conductivity due to the conformational flexibility of the linear substituents
- stability enhancement is not quite enough to enable sustained CO_2 reduction

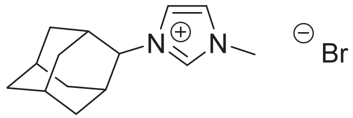


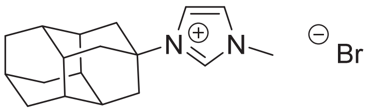
- greater stability by preventing the reactive centers in cations from approaching as closely to electrode surfaces
- may enhance ion conductivity by providing voids, channels, and/or pathways for ion transport
- interesting for gas adsorption applications, due to the presence of packing 'voids' within the liquid

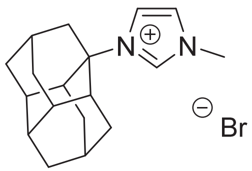
Diamondoid IL

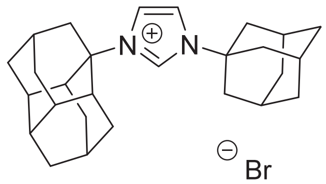




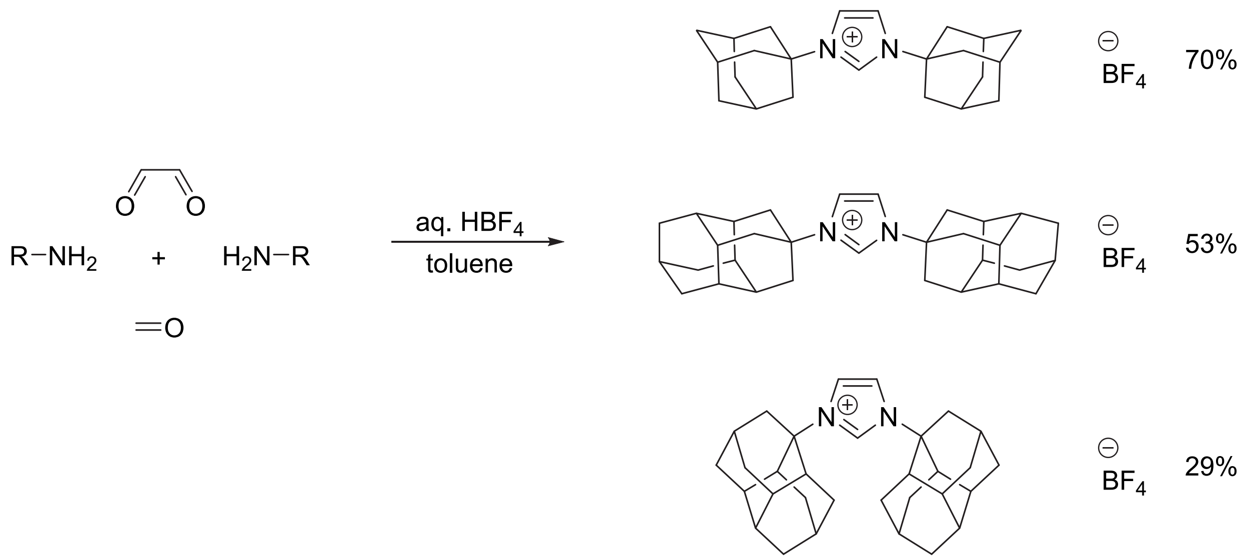




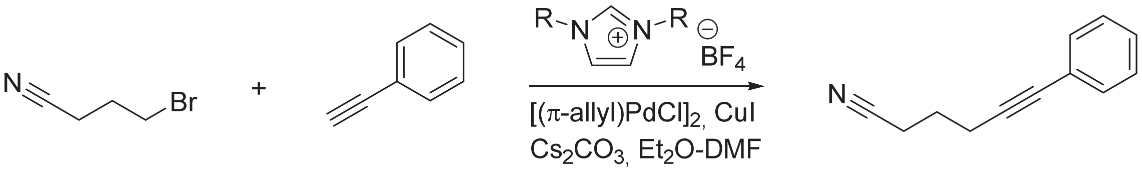




Diamondoid Imidazolium Salts as Precursors for N-heterocyclic Carbenes



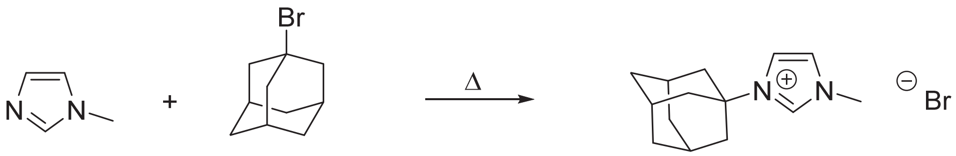
Sonogashira Coupling

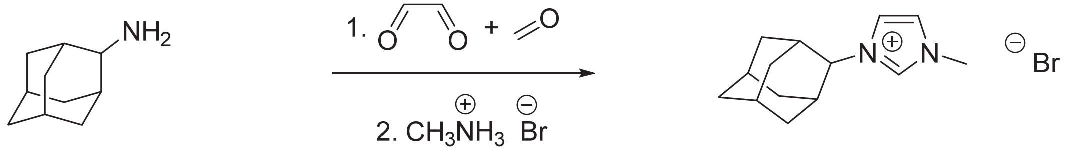


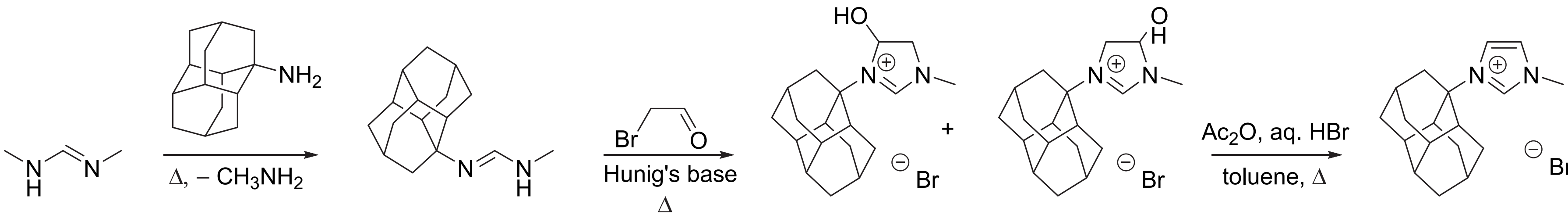
R = 1-Ad	74%
1-Diam	88%
4-Diam	76%

H. Richter, H. Schwertfeger, P. R. Schreiner, R. Fröhlich, F. Glorius, *Synlett* **2009**, *2009*, 193-197.

Proposed Diamondoid IL Synthesis







L. Ming, N. Martin, H. E. G., S. Andreas, *Chem.–Eur. J.* **2016**, *22*, 5416-5424,
R. M. Nageswar, H. Meera, G. M. Kumar, R. Palanisamy, K. A. Ch., G. Prasenjit, *Eur. J. Inorg. Chem.* **2015**, *2015*, 1604-1615,
S. M. Bronner, M. B. Herbert, P. R. Patel, V. M. Marx, R. H. Grubbs, *Chemical Science* **2014**, *5*, 4091-4098.

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The PRS group

Thank you for your attention!