Ionic Liquids: a new "solution" for solution chemistry ?

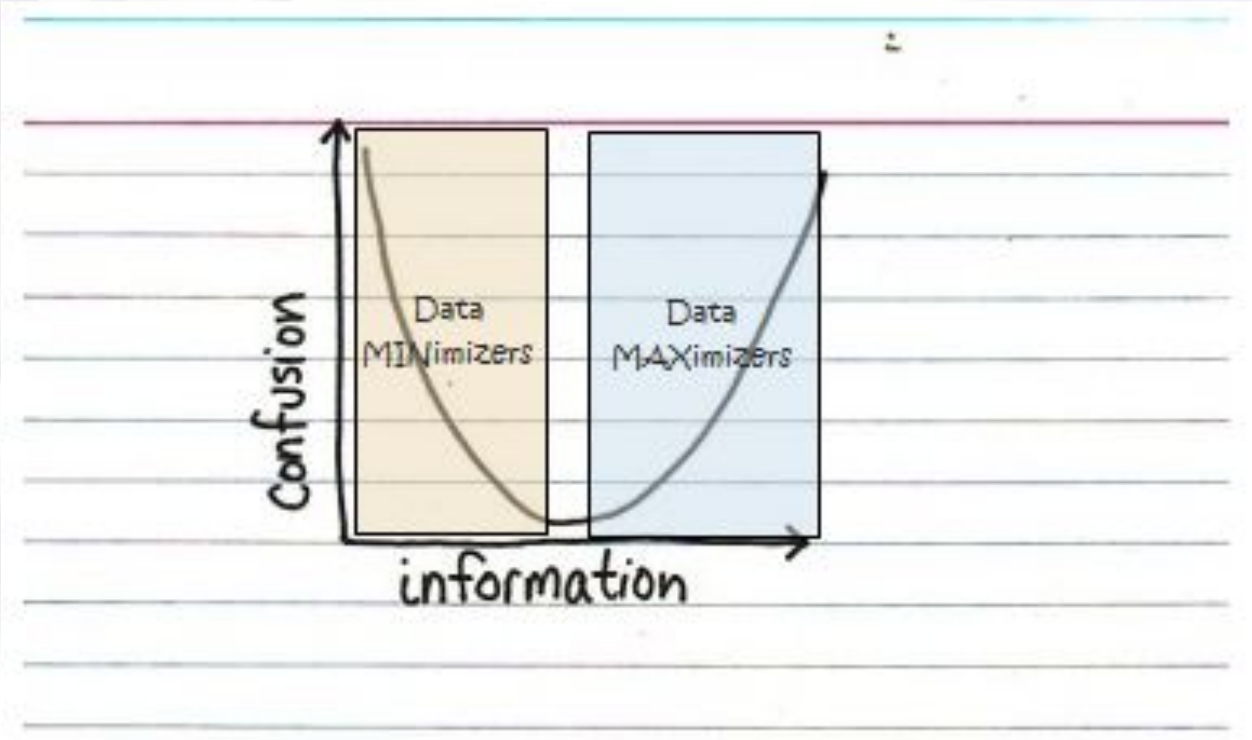
Jairton Dupont
Laboratory of Molecular Catalysis
Institute of Chemistry – UFRGS


Porto Alegre

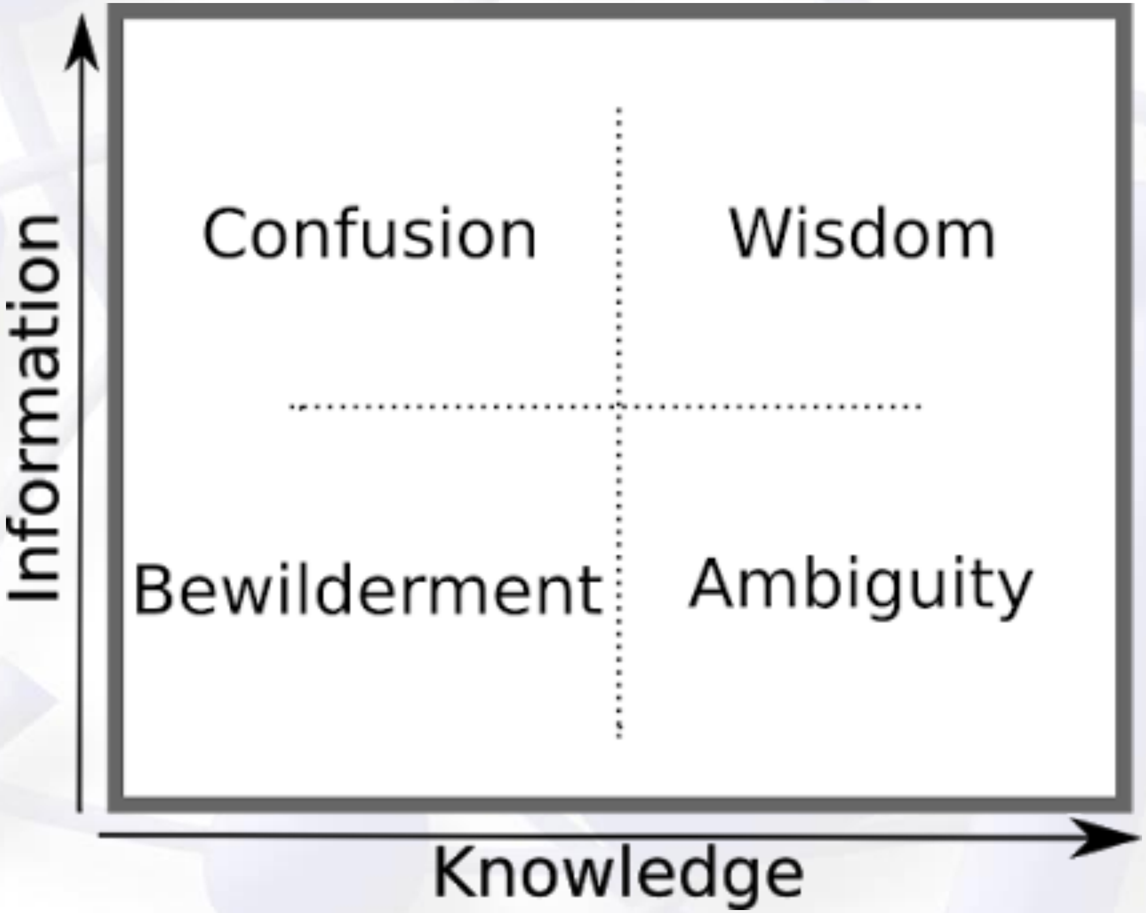

VEN.
GUY.
SUR.
COL.
Boa Vista
Equator
Pico da Neblina
Belém
NORTH ATLANTIC OCEAN
São Luís
Manaus
Amazon
Fortaleza
Teresina
Natal
Rio Branco
Recife
Maceió
PERU
Salvador
BRASÍLIA
BOLIVIA
Campo Grande
Belo Horizonte
Tubarao
Vitória
São Paulo
Rio de Janeiro
PARA.
CHILE
Curitiba
Santos
Sepetiba Terminal
SOUTH PACIFIC OCEAN
Porto Alegre
SOUTH ATLANTIC OCEAN
ARGENTINA
URU.
0 300 600 km
0 300 600 mi

Rio Grande do Sul - Brazil





confusion
Data
MINimizers
Data
MAXimizers
information


Information
Confusion
Wisdom
Bewilderment
Ambiguity
Knowledge

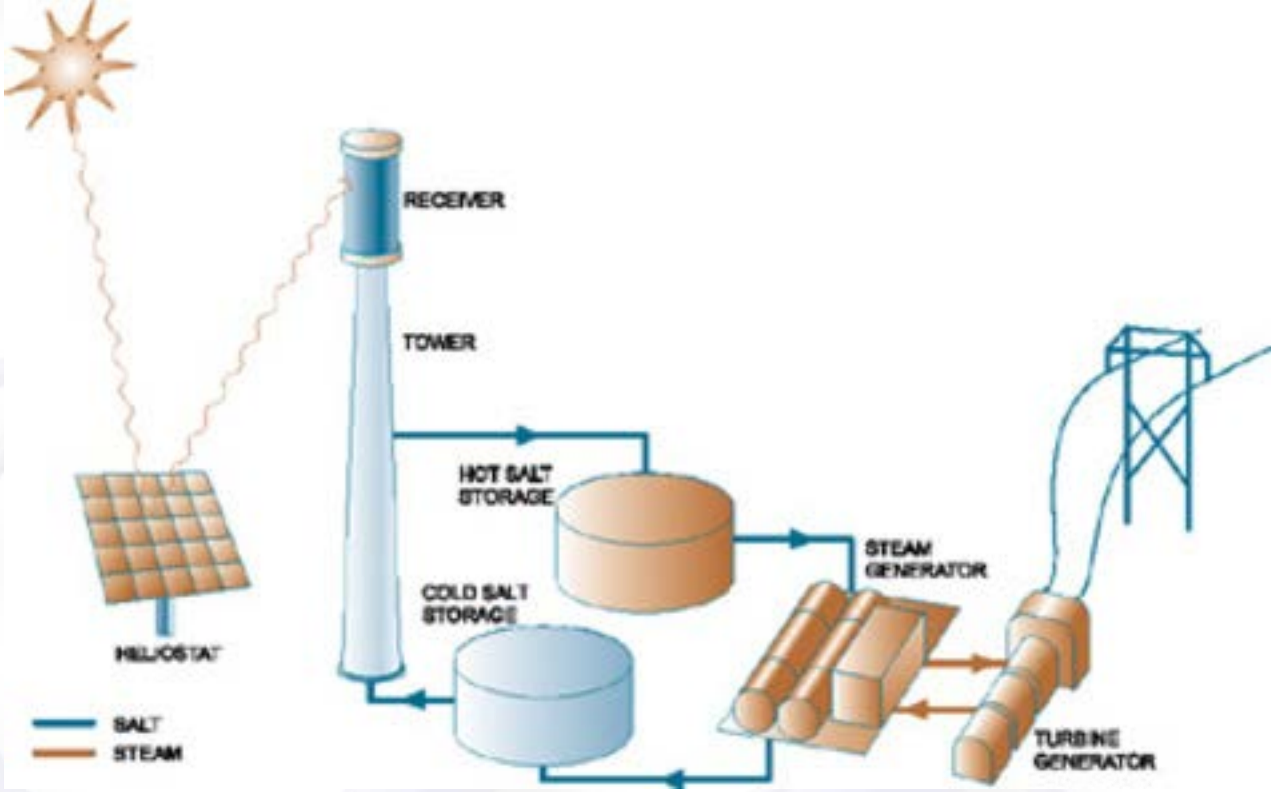
Molten Salts

Any liquid electrolyte composed entirely of ions is denominated a molten salt or a fused salt

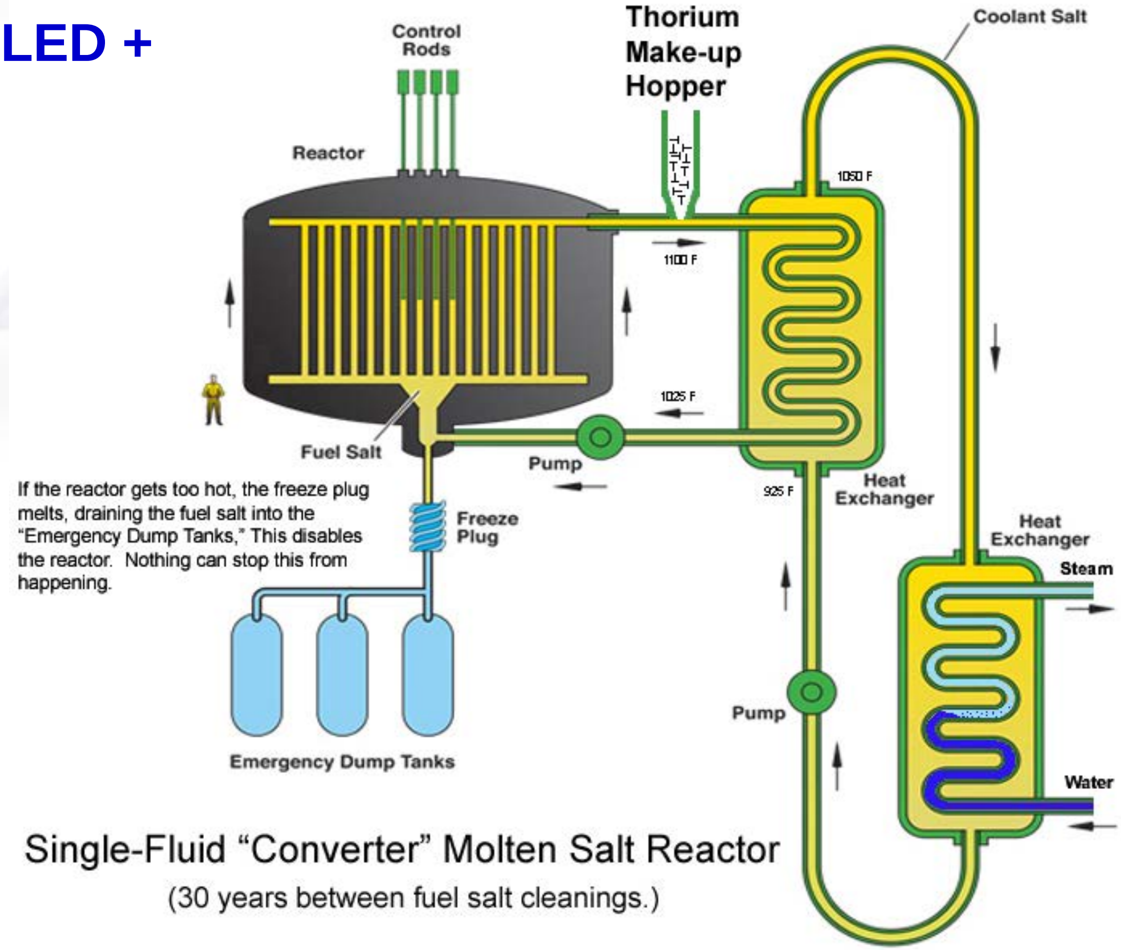
Type	Example	m.p. (ºC)
Inorganic	NaCl	801
Organic	$(^{n}Bu)_4PCl$	80
Eutectic	LiCl/KCl (6/4)	352
Organomineral	$Et_3NHCl/CuCl$	25

UFRGS

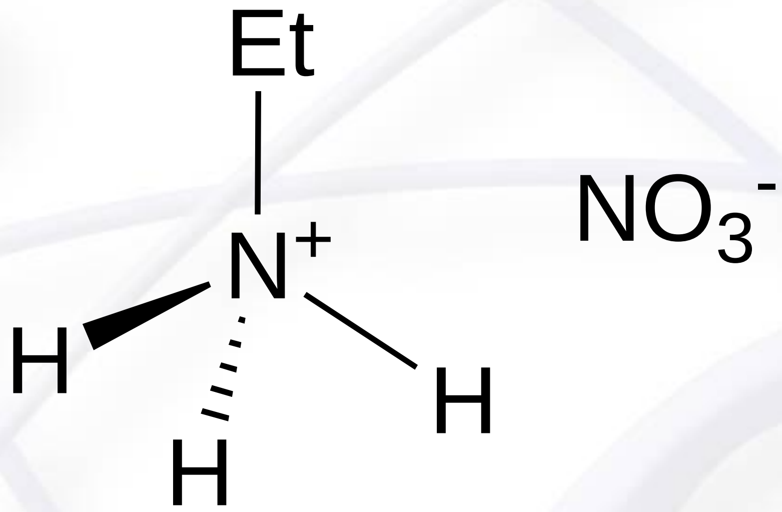
Solar Plants



MAGIC TEAM: THORIUM-FUELED + MOLTEN SALT REACTORS



Single-Fluid "Converter" Molten Salt Reactor
(30 years between fuel salt cleanings.)



mp= 12 ºC

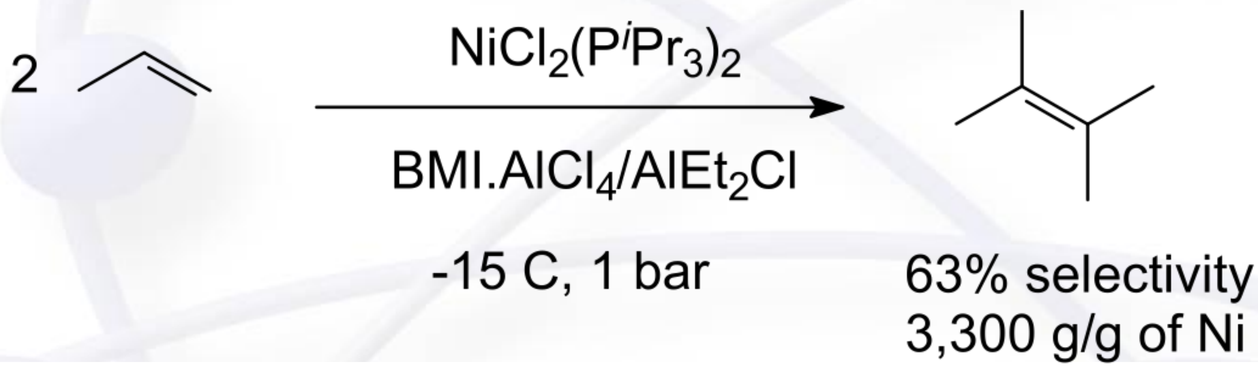
Walden, P. *Bull. Acad. Imper. Sci. (St. Petersburg)* ***1914, 405. C.A. 1914, 8, 2291***

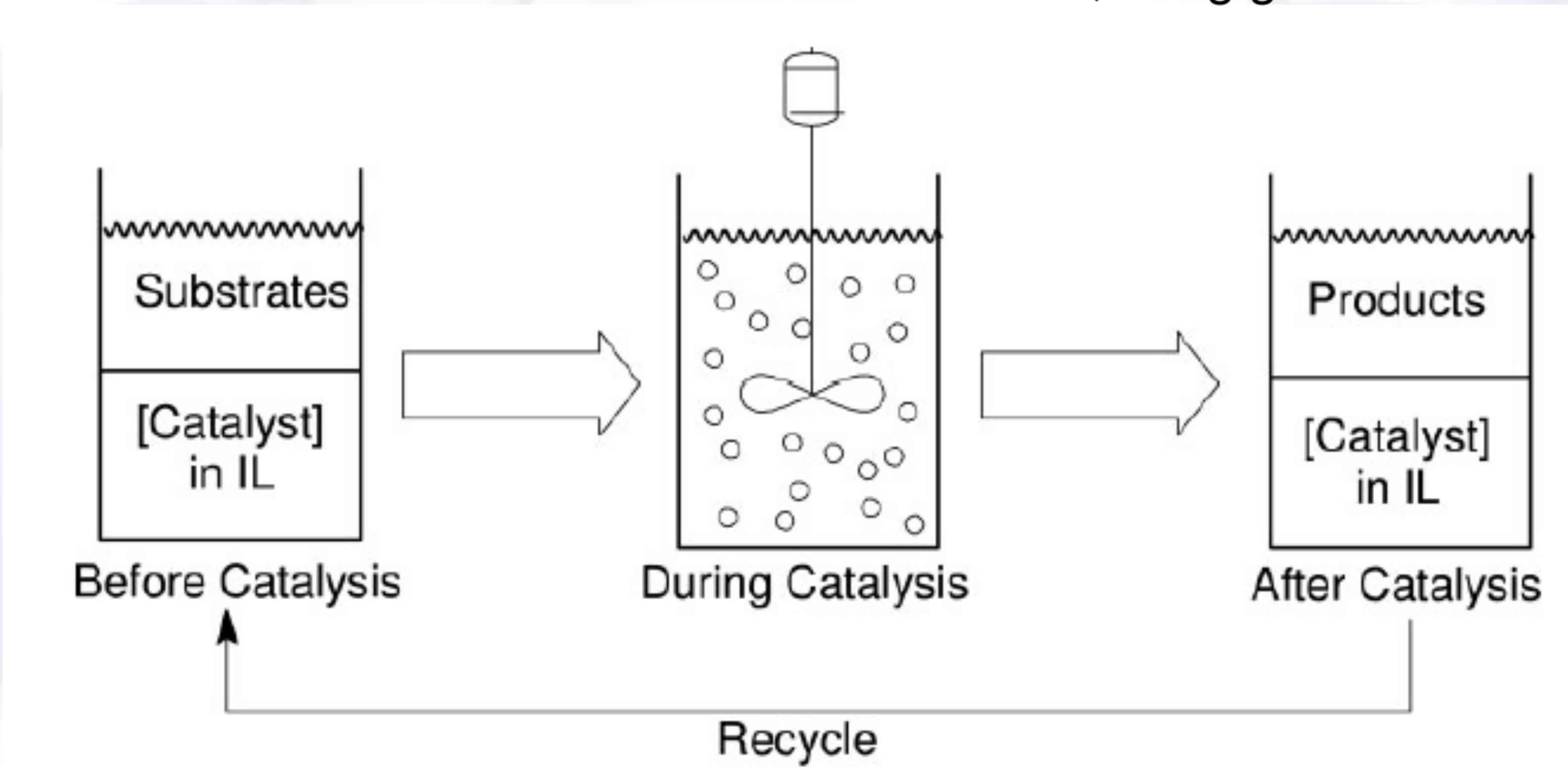
Ionic Liquids

"Non-corrosive" molten salts that are
fluid below 100ºC and posses relatively low viscosity

mp= 77-79 °C mp= 190 °C mp= -88 °C

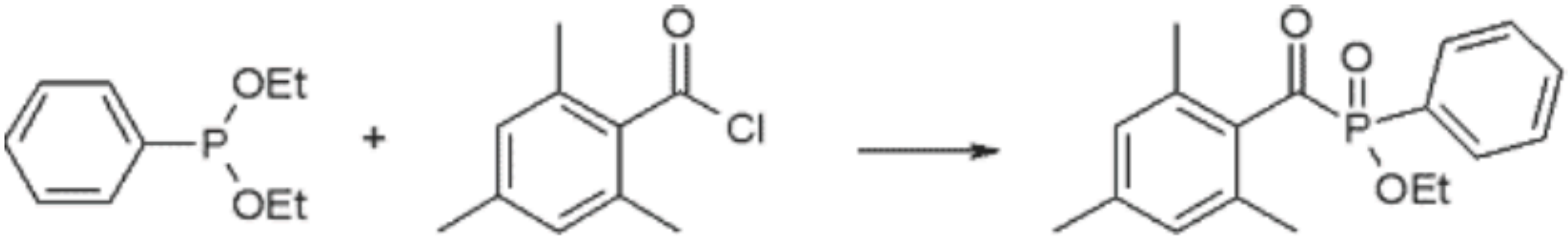
F. H. Hurley, T. P. Wier, *J. Electrochem. Soc.* **1951**, *98*, 203.





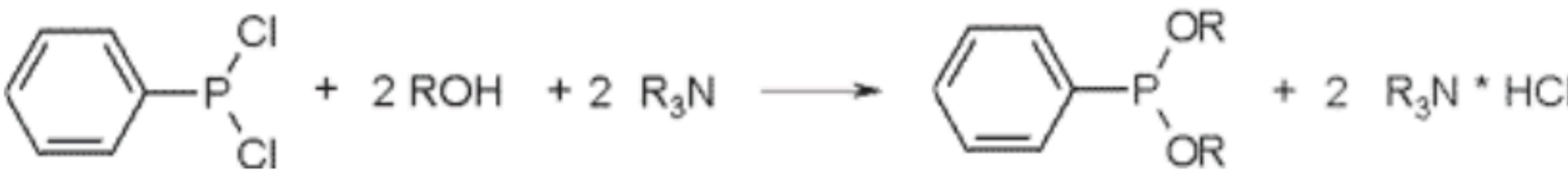
Chauvin, Y.; Gilbert, B.; Guibard, I. *J. Chem. Soc., Chem. Commun.* **1990**, 1715.

BASIL - BASF

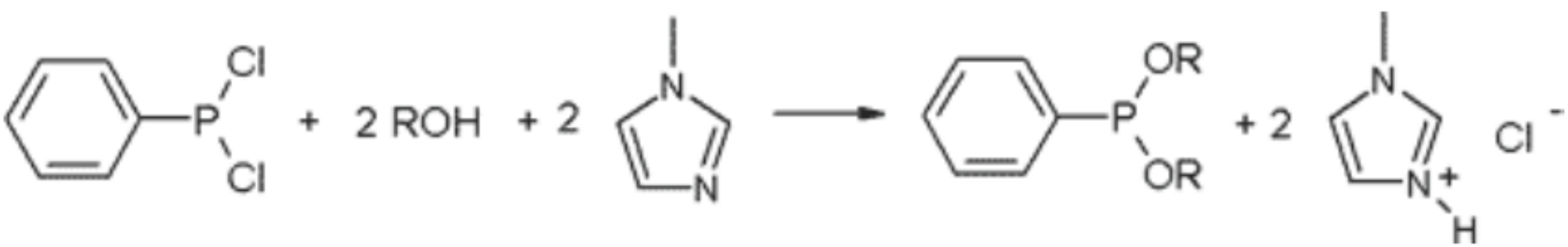


Scheme 1: Synthesis of Lucirin® TPO-L

HCl is formed during the synthesis of diethoxyphenylphosphine (Scheme 2).



Scheme 2: Synthesis of Dialkoxyphenylphosphines



Scheme 3: 1-methylimidazole as an acid scavenger

Today the BASIL™ process is run in a little jet stream reactor which has a capacity of 690000 kg m^{-3} h^{-1}.

Scheme 1: Chlorination of alcohols with HCl gas

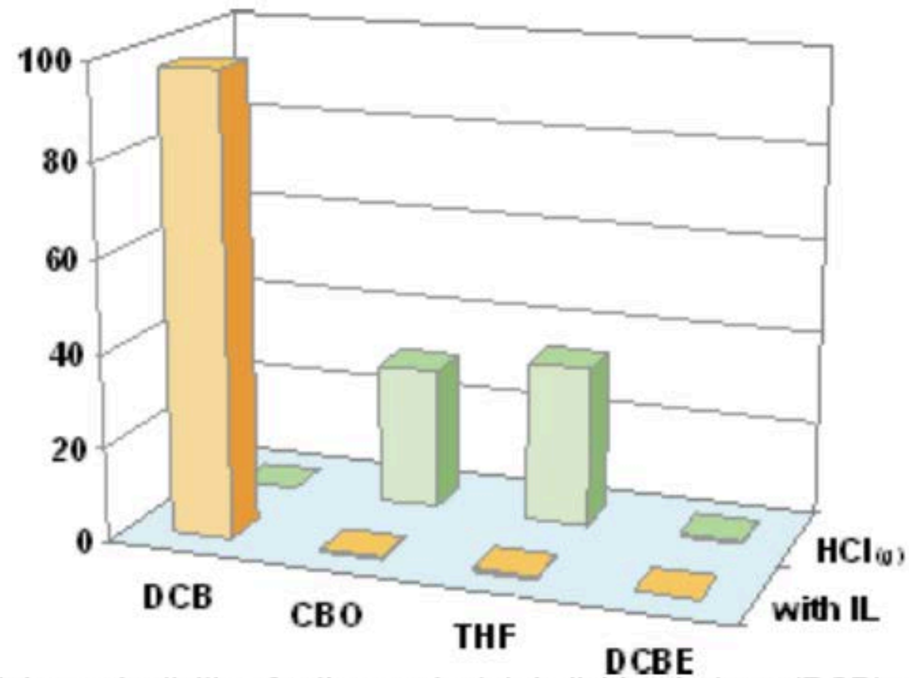
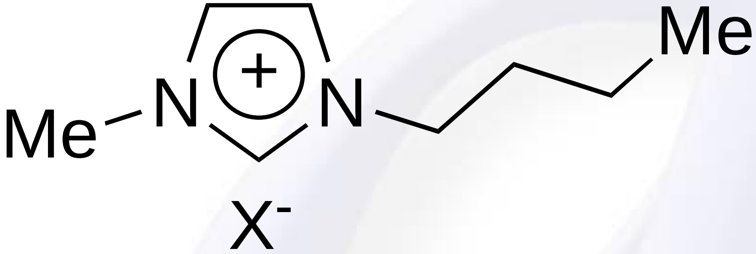


Figure 1: Higher selectivities for the product 1,4-dichlorobutane (DCB) are achieved if the chlorination of the butanediol with HCl gas is performed in an ionic liquid rather than in the pure alcohol. Side products usually are ethers (tetrahydrofurane THF, dichlorobutylether DCBE) or the monochlorinated product 1-chlorobutane-4-ol (CBO).

BF_4^- mp= 15 ºC

J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1992**, 965.



mp= down to -80 ºC

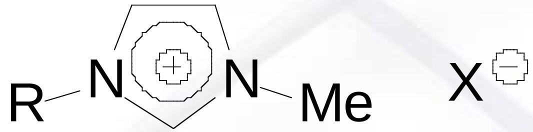
P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. deSouza, J. Dupont, *Polyhedron* **1996,** *15* 1217-1219. (Received 16 June 1995).

Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem. Int. Ed. Engl.* **1995,** *34* 2698-2700. (Received 18 August 1995).

P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1996,** *35* 1168-1178. (Received 15 August 1995).

UFRGS

Physical-chemical properties



R	X	Tg[a] (ºC)	Tm[b] (ºC)	Td[c] (ºC)	η (mPa s)[d]	*d* (g.cm^{-3})[e]	σ (mScm^{-1})[f]
Et	BF_4	-92	13	447	37	1.28	14
^{n}Pr	BF_4	-88	-17	435	103	1.24	5.9
^{n}Bu	BF_4	-85	none	435	180 (233)	1.21	3.5 (8.6)
^{n}Bu	PF_6	-61	10	-----	219 (312)	1.37	1.6 (6.5)
^{n}Bu	$AlCl_4$	-88	none	----	(294)	1.23	(24.1)
^{n}Bu	CF_3SO_3	----	16	-----	90	1.22	3.7
^{n}Bu	$N(Tf)_2$	----	-4	>400	69	1.43	3.9
^{n}Bu	CF_3CO_2	-30	none	-----	73	1.21	3.2
Ethylene glycol		none	-13	196[g]	21	1.11	-----

[a] Transition glass temperature, [b] Melting point, [c] Decomposition temperature, [d] Viscosity at 25°C and in parenthesis at 30°C, [e] Density at 25°C, [f] Conductivity at 25°C and in parenthesis at 60 °C, [g] boiling point.

Dupont, J. *J. Braz. Chem. Soc.* **2004**, *15*, 341.

UFRGS

Ionic Liquids

- No measurable vapour pressure
- High chemical and thermal stability
- Large electrochemical window (up to 7V)
- Relatively low viscosity (2-3 poises)
- Variable solubility with organic compounds

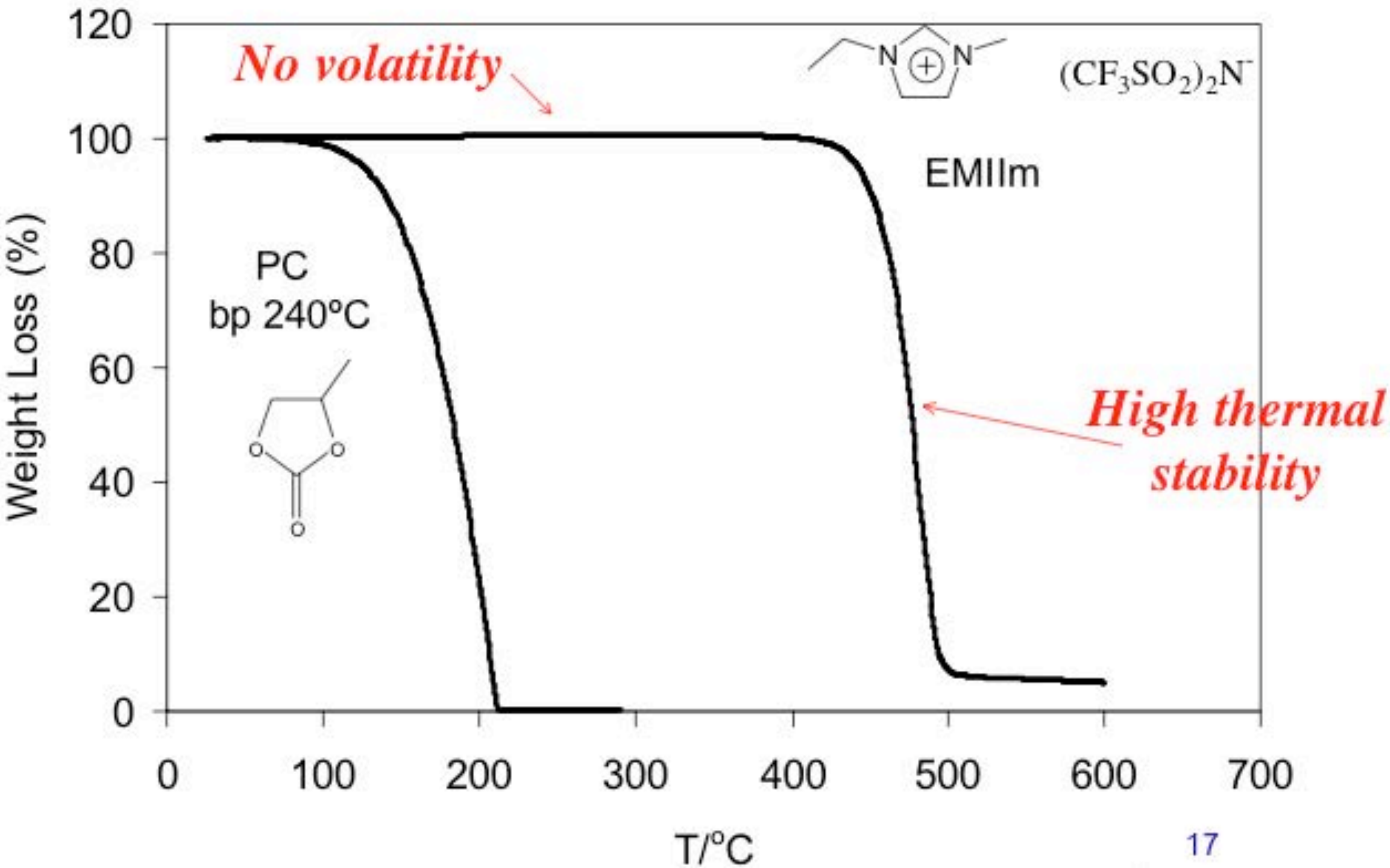
Chem. Rev. **2002**, *102*, 3667.

Vapor Pressure

Organic Solvent

Water

Critical Thermal Stability



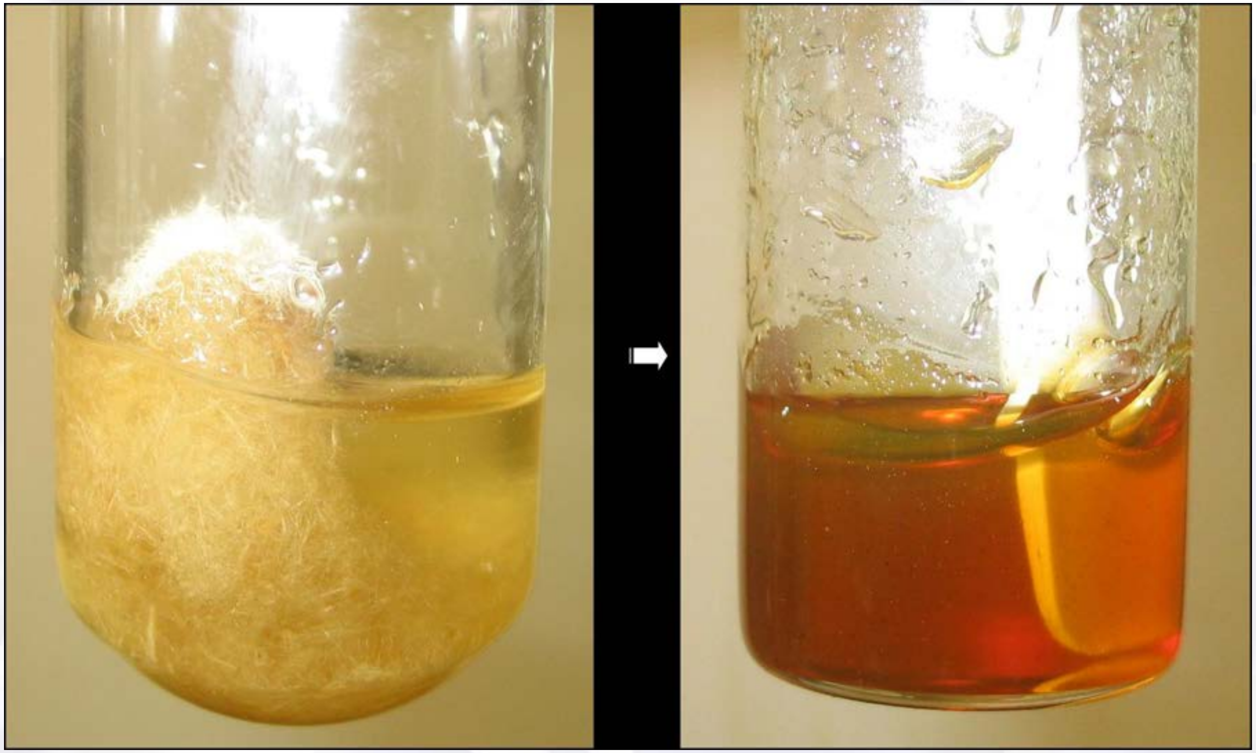
Covalent Associates, Inc.

New Applications

Lubricants

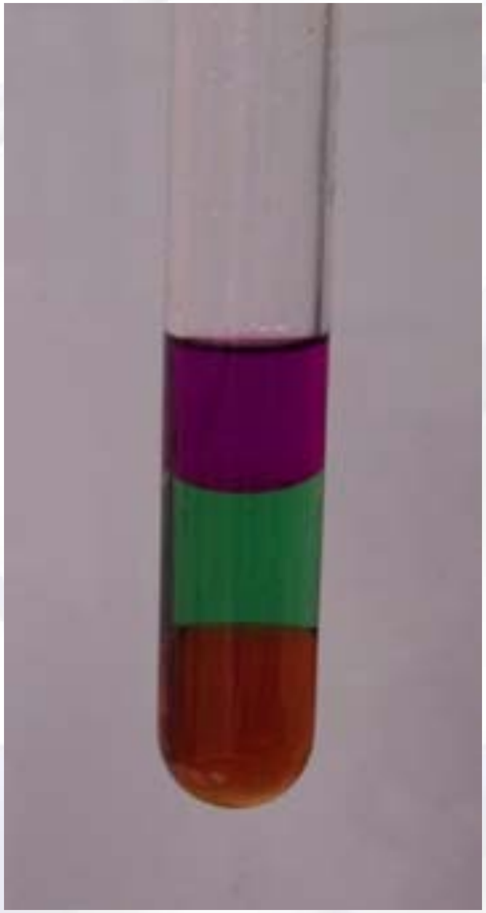
Electrical rubber as synthetic skin for robots made by grinding carbon nanotubes with an ionic liquid and adding it to rubber

Solubilization



Pine wood fibers in ionic liquid

Miscibility

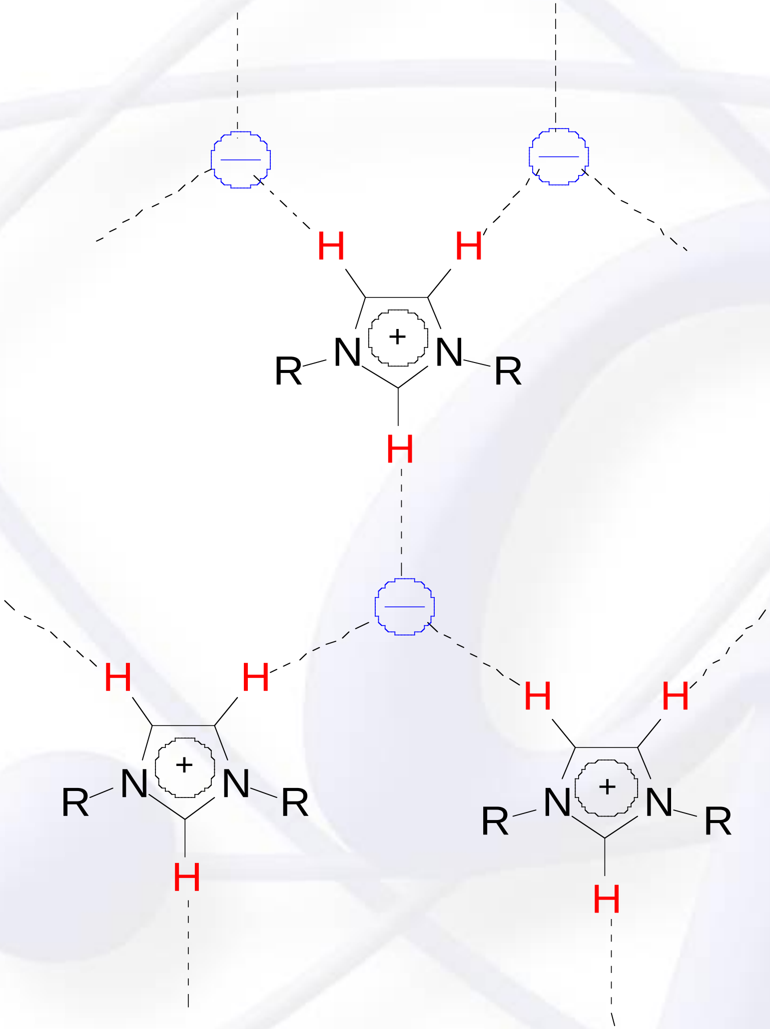


N-octane

Water

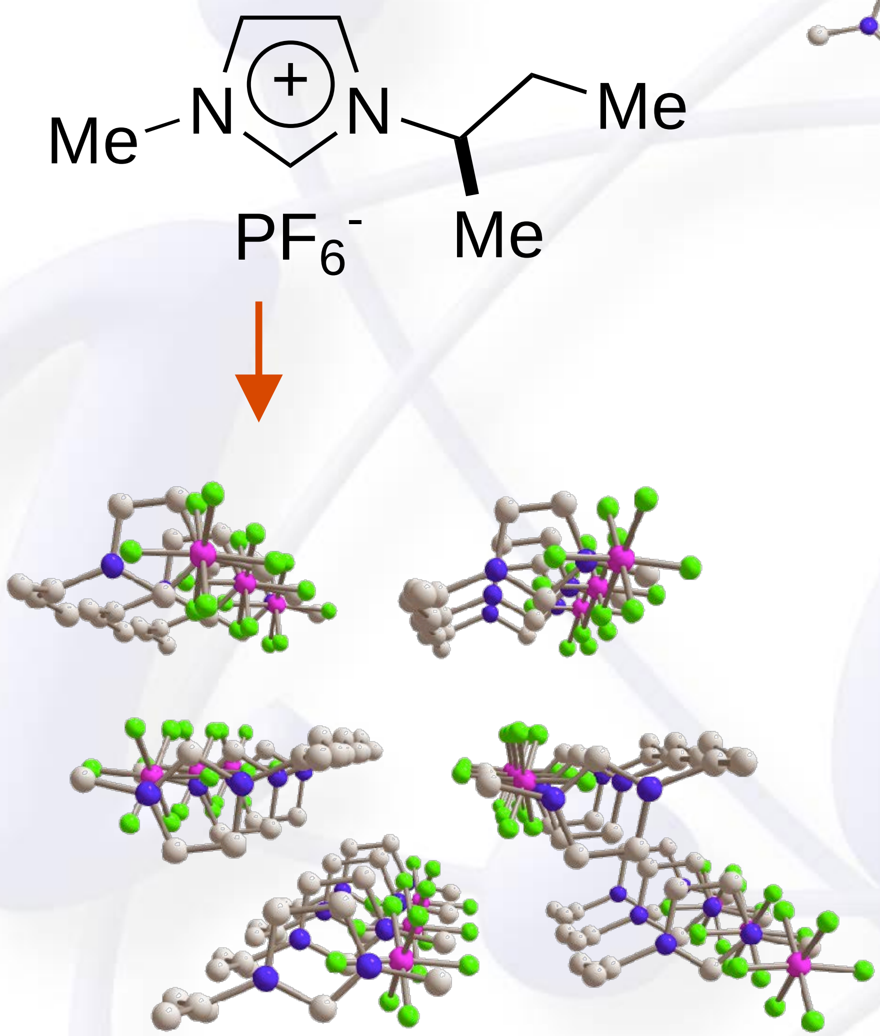
Ionic Liquid

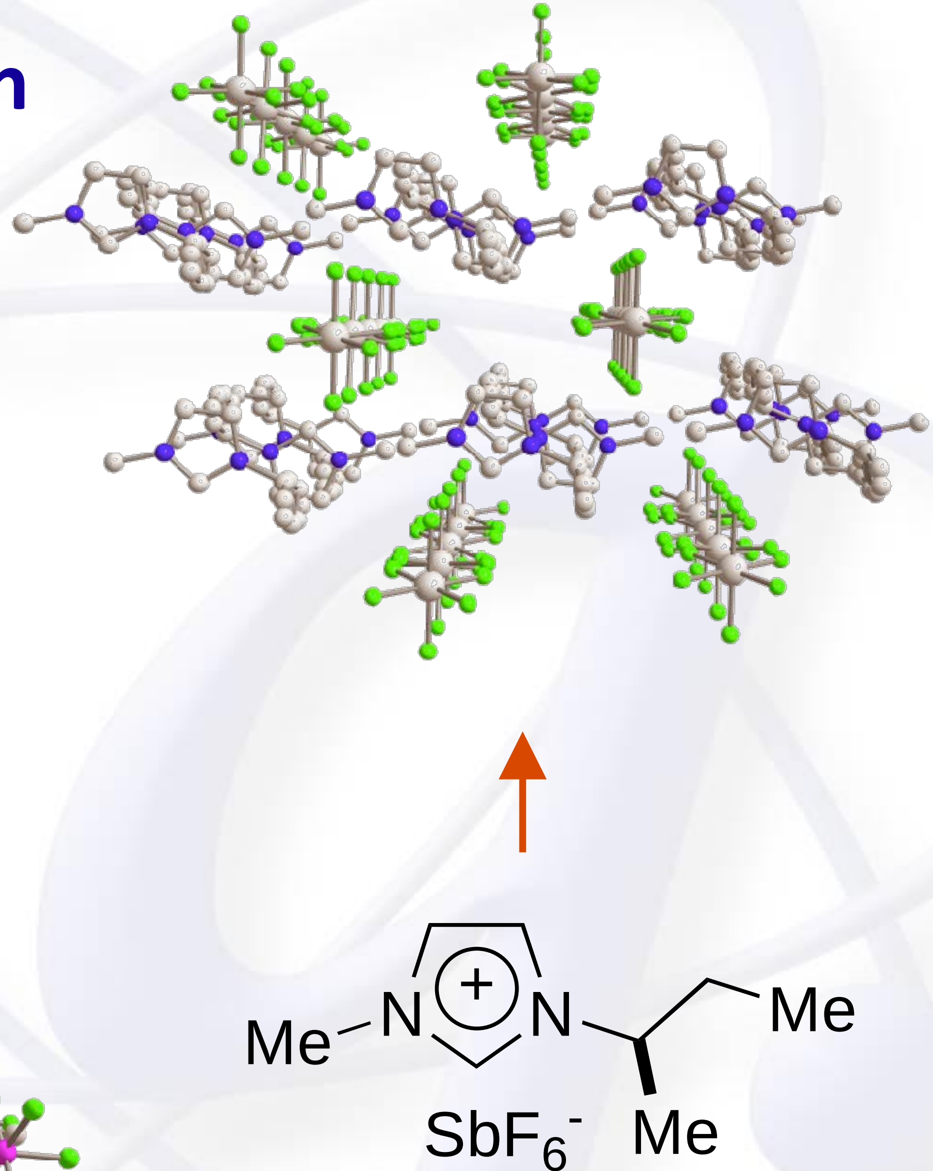
Structural Organization of Imidazolium Ionic Liquids



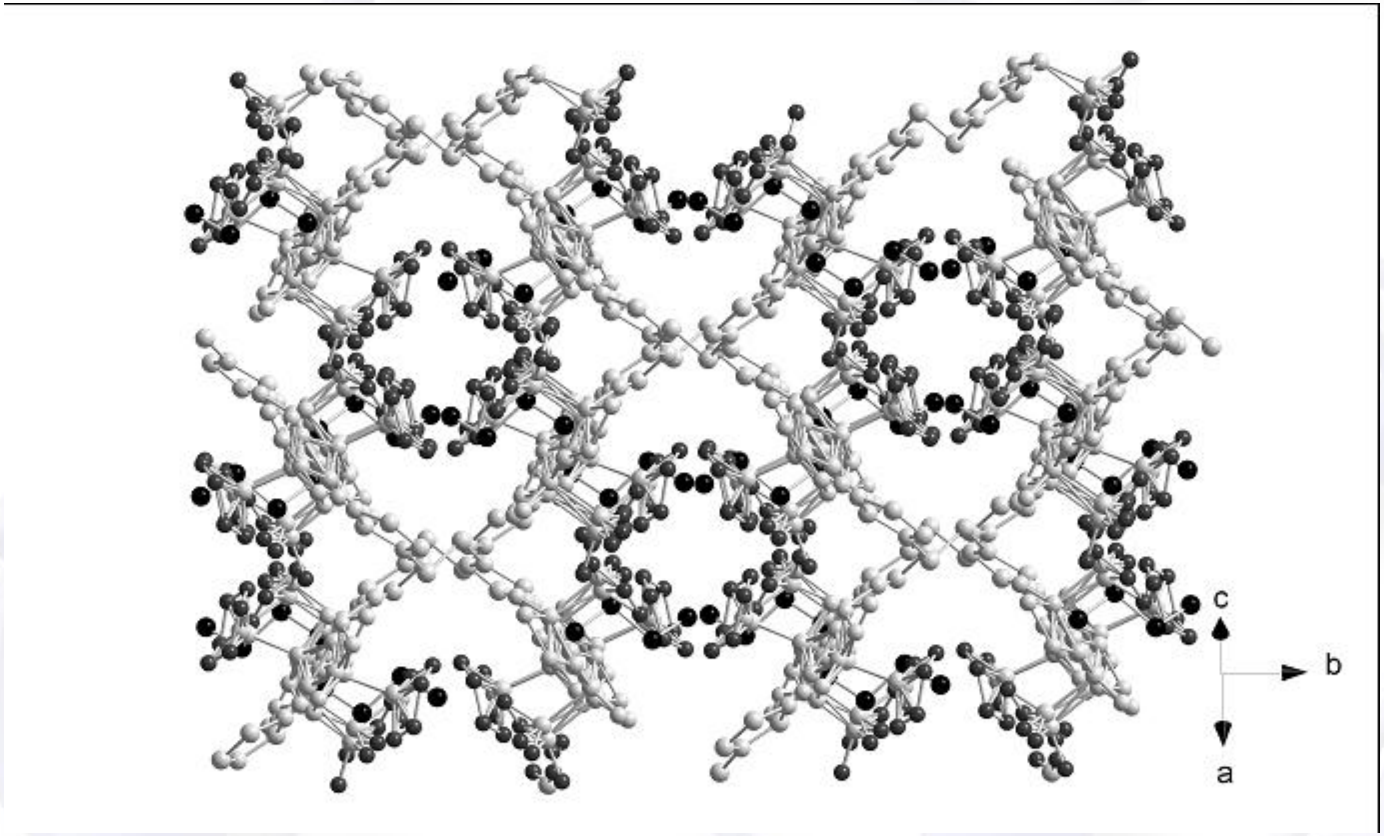
Chem. Phys. Phys. Chem **2006**, *8*, 2441
Chem. Eur. J. **2000,** *6*, 2377

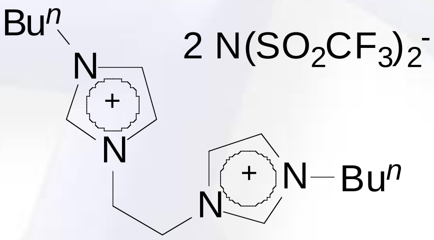
Solid State Organization





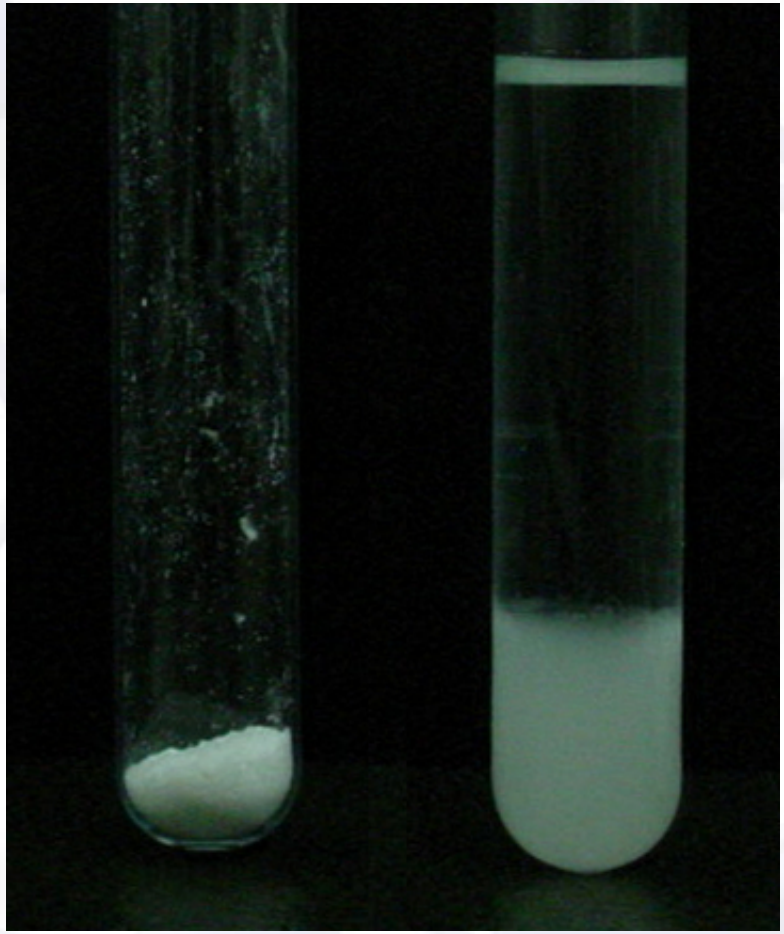
C. Consorti, 2002

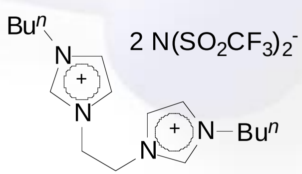




View of the crystal structure of **dicationic ionic liquid** through the crystallographic *h,k,l* (7.54, 0, 12.8) plane. Hydrogen atoms have been omitted for clarity; fluorine atoms and butyl groups shown in dark gray.

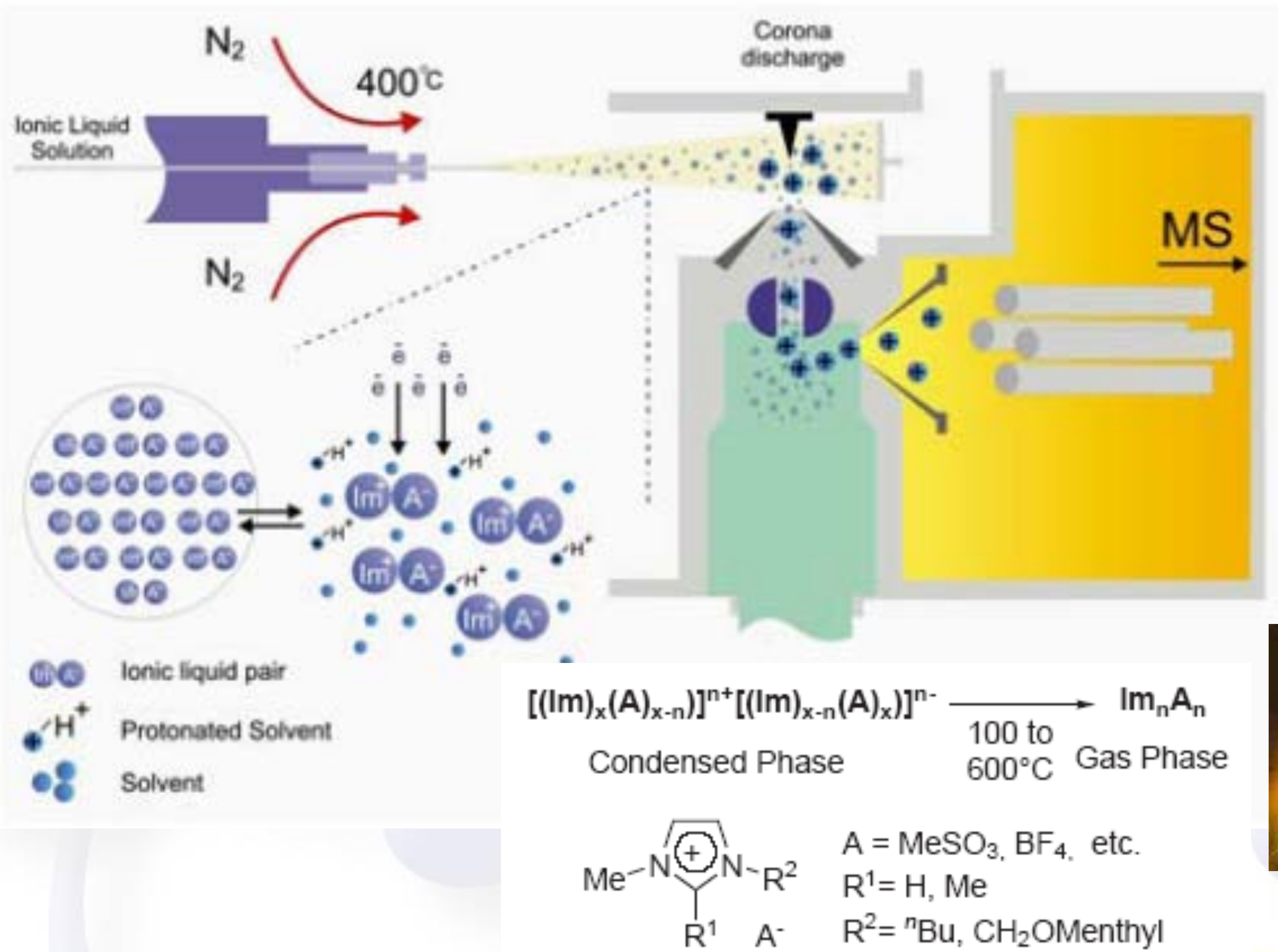
F. Rominger, C. C. Cassol, unpublished results





in n-octane

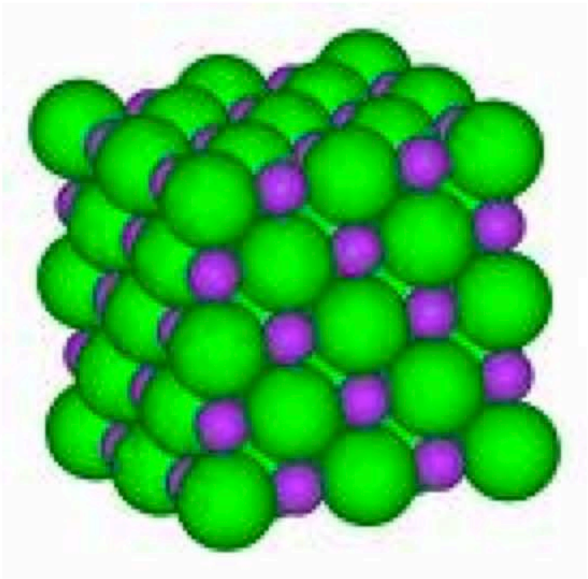
Gas Phase Structural Organization



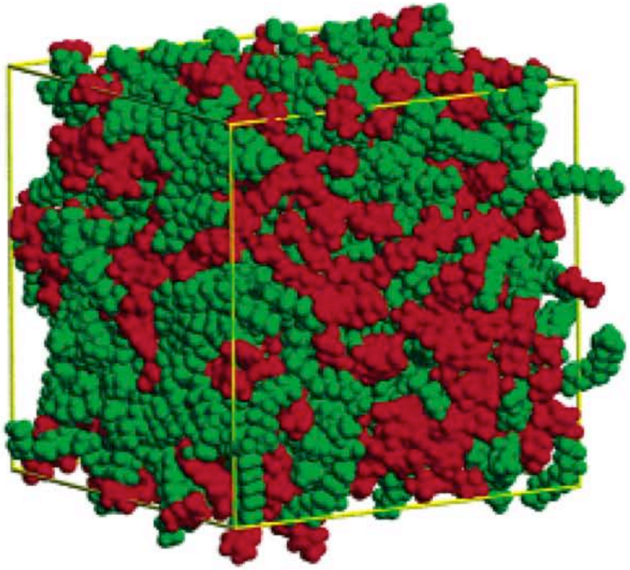
Angew. Chem. Int. Ed. **2006**, *45*, 7251

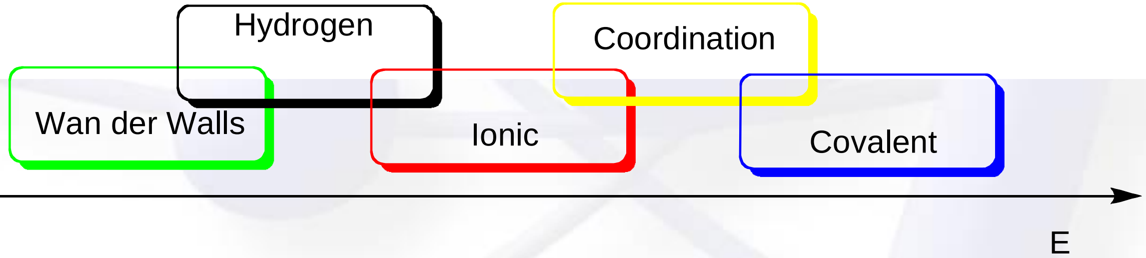
IONIC LIQUIDS

Classical



"Modern"





Acc. Chem. Res. ***2011,*** *44*, 1223-1231

Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(*S*)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids

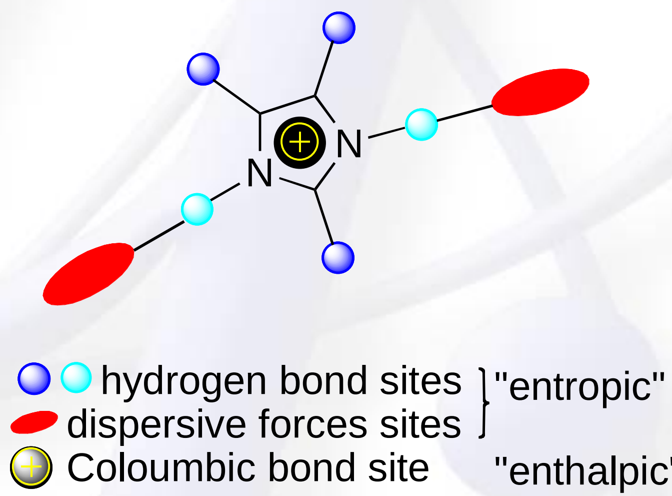
Uwe Schröder,[a] Jay D. Wadhawan,[a] Richard G. Compton,[a] Frank Marken,*†[a]
Paulo A. Z. Suarez,[b] Crestina S. Consorti,[b] Roberto F. de Souza[b] and Jaïrton Dupont[b]

Conclusions

It has been shown that traces of water can have a dramatic effect on the electrochemical characteristics and the rate of diffusion observed voltammetrically in ionic liquid media. In particular, the contrast in the effect of water on the diffusion coefficient for neutral and for ionic species suggests that 'wet' ionic liquids may not be regarded as homogeneous solvents, but have to be considered as 'nano-structured' with polar and non-polar regions.

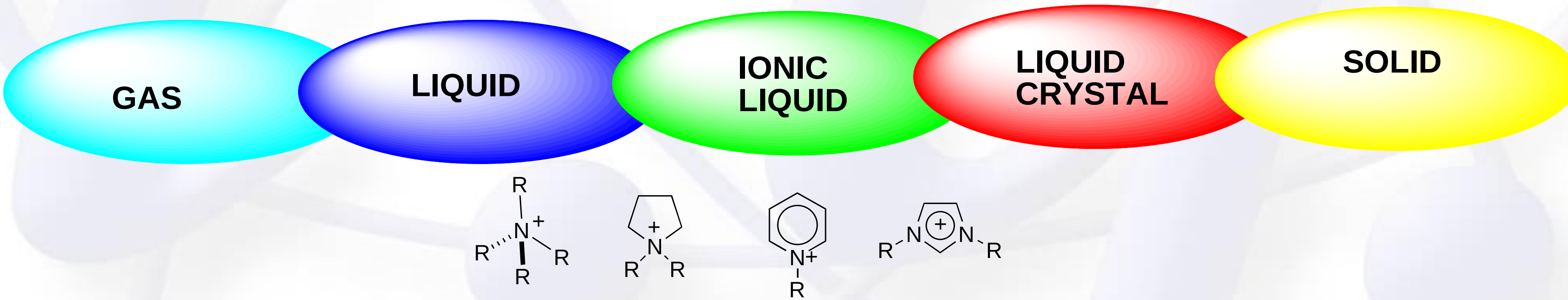
New J. Chem., 2000, **24**, 1009–1015

Directionality imposed mainly by weak interacitions

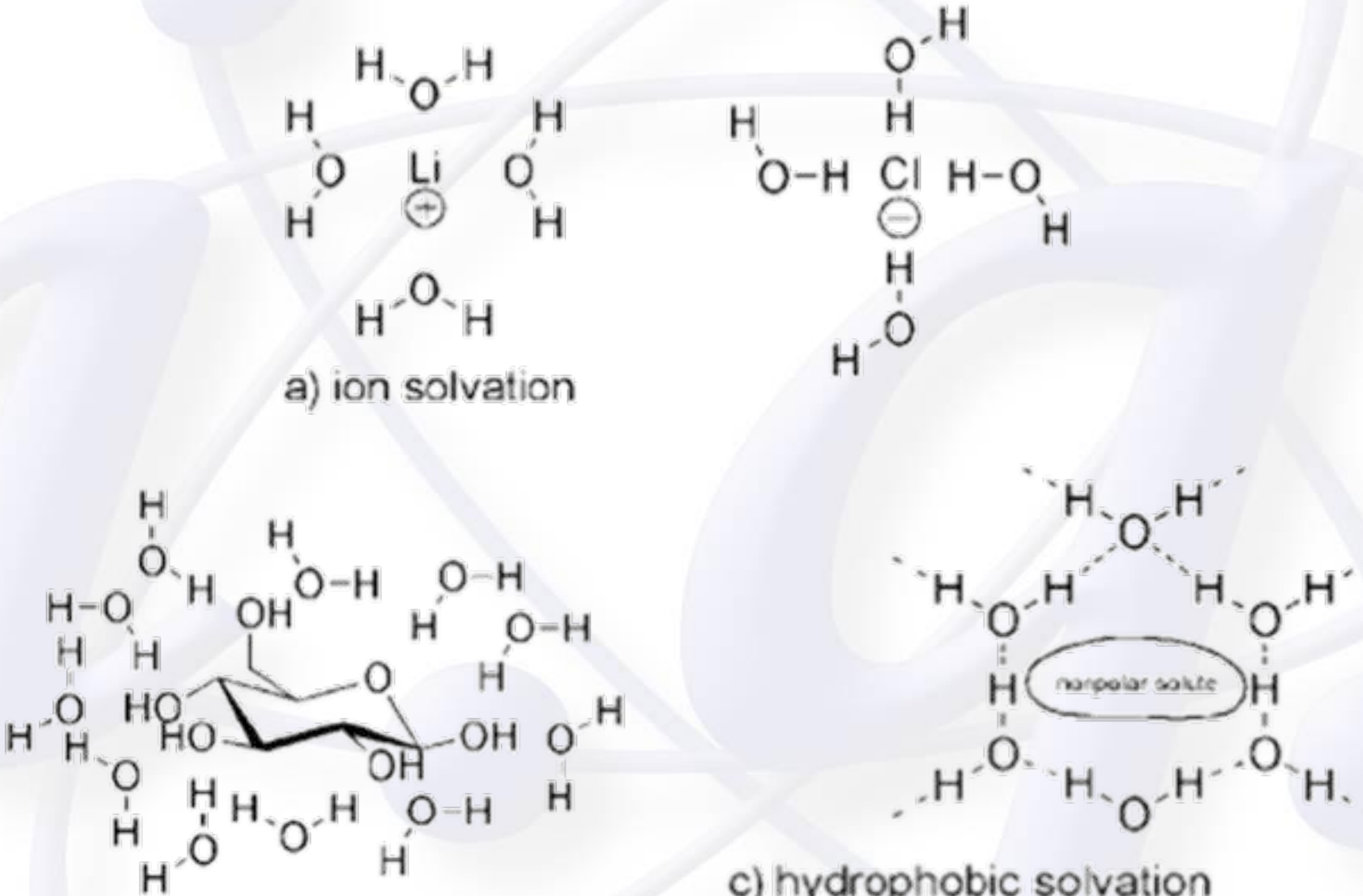


Acc. Chem. Res. **2011**, *44*, 1223

ILs cannot be regarded as merely homogeneous solvents. In fact, ILs form extended hydrogen-bond networks with polar and non-polar nano domains and therefore are by definition “supramolecular” fluids.



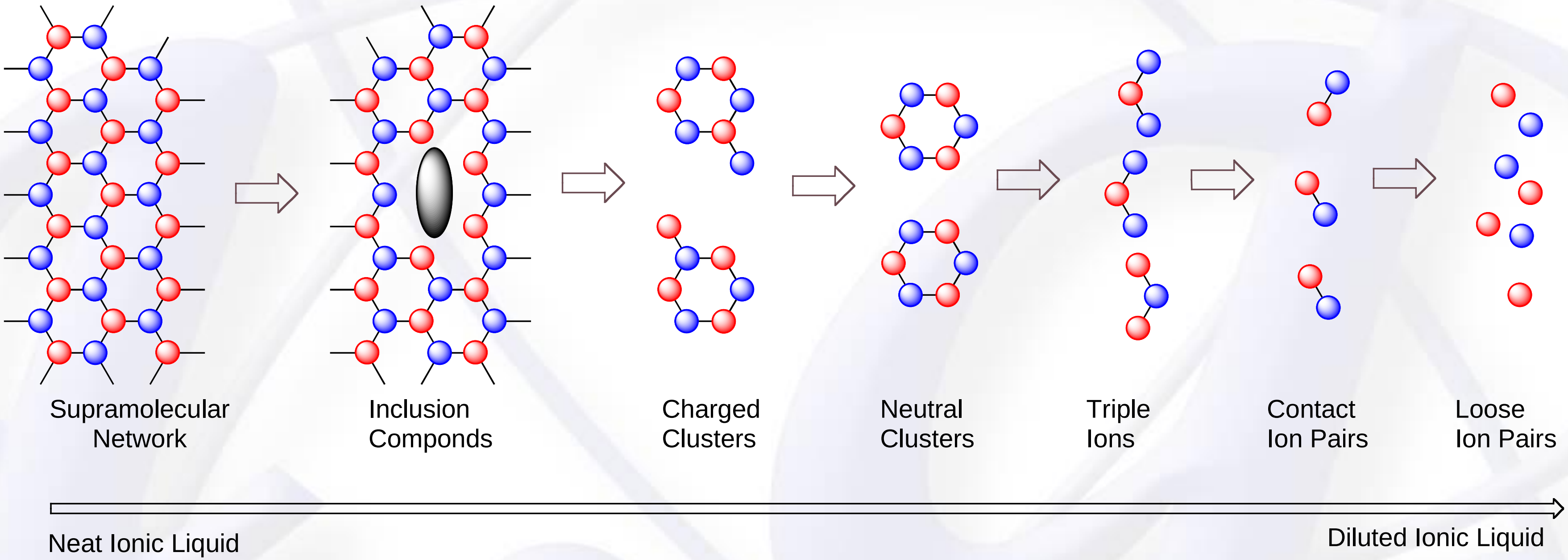
Different Modes of Aqueous Solvation



a) ion solvation

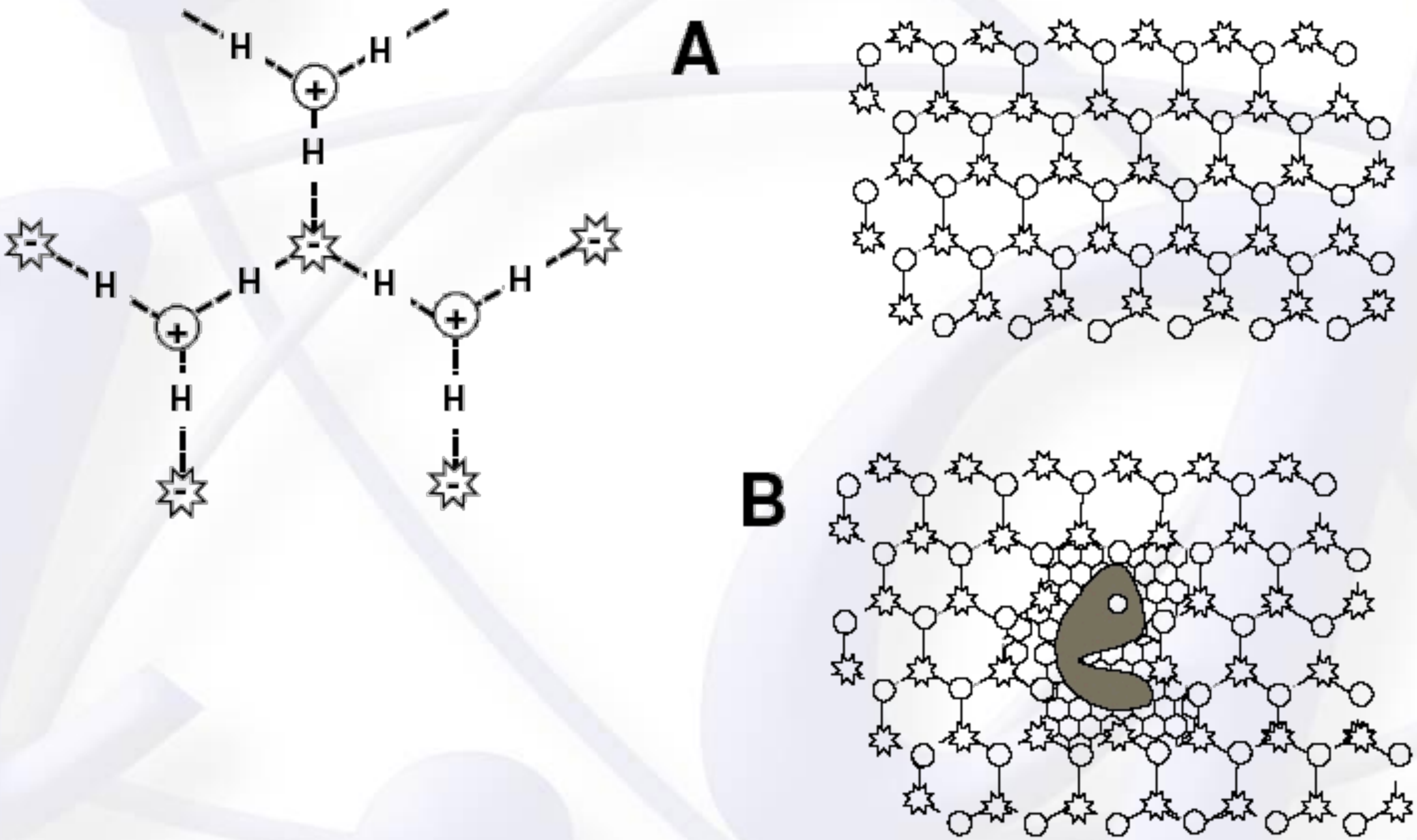
b) hydrogen-bond solvation

c) hydrophobic solvation



J. Braz. Chem. Soc. **2004**, *15*, 341

“Inclusion” Enzyme Complex



A. Two-dimensional simplified model of the supramolecular structure of imidazolium ILs based on hydrogen bond interactions. B. Schematic description of the “inclusion” of enzymes in wet regions into the IL network.

P. Lozano, 2005, Murcia

Imidazolium Ionic Liquids

Pure form: Polymeric supramolecules with weak interactions

$\{[(DAI)_3(X)]^{2+}[(DAI)(X)_3]^{2-}\}_n$

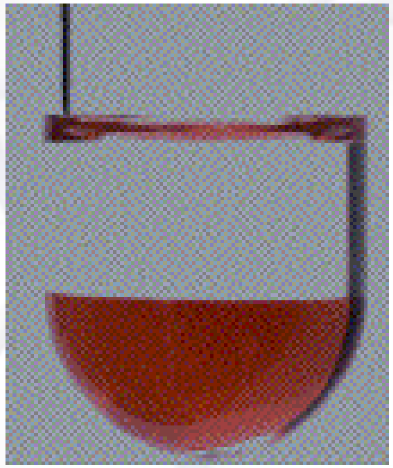
Mixture: Nanostrutured materials

$[(DAI)_x(X)_z]^{x-z}\ [(DAI)_y(X)_x]^{x-z}$

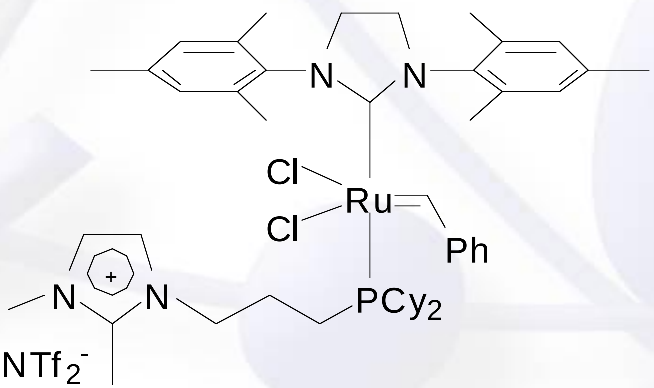
$x>1$ and $z>0$

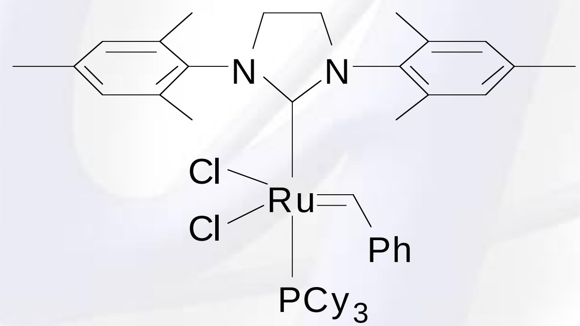
J. Braz. Chem. Soc. **2004**, *15*, 341.
J. Phys. Chem. B **2005**, *109*, 4341

Ionophilic Ligands/Complexes: Multiphase Catalysis

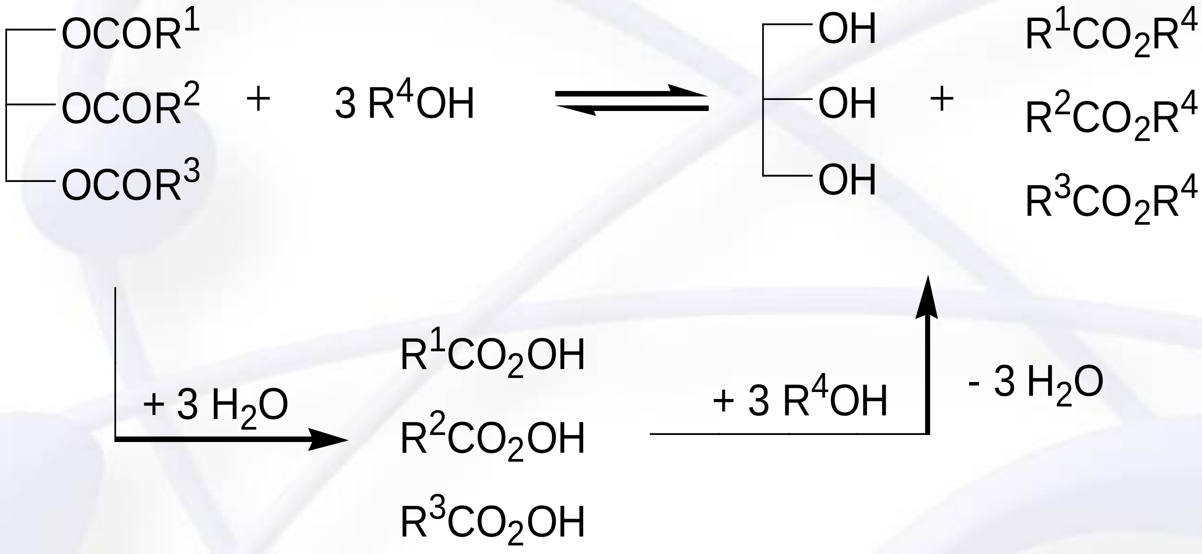


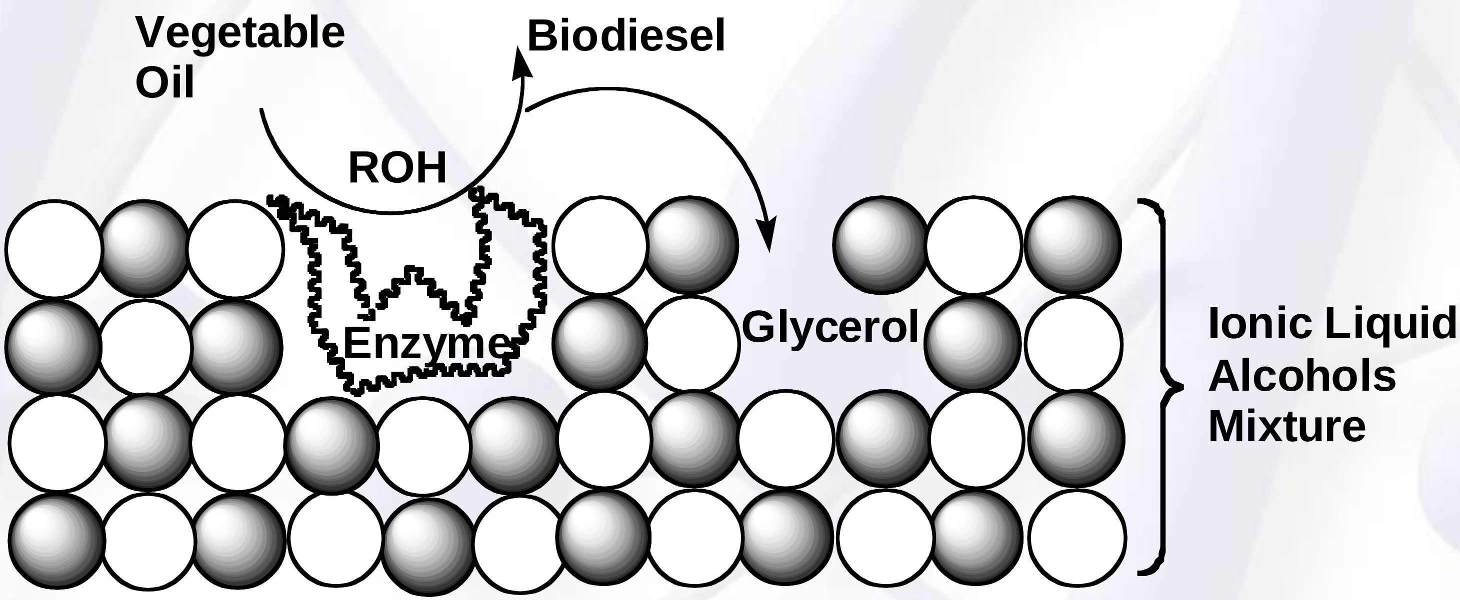
$BMI.PF_6$





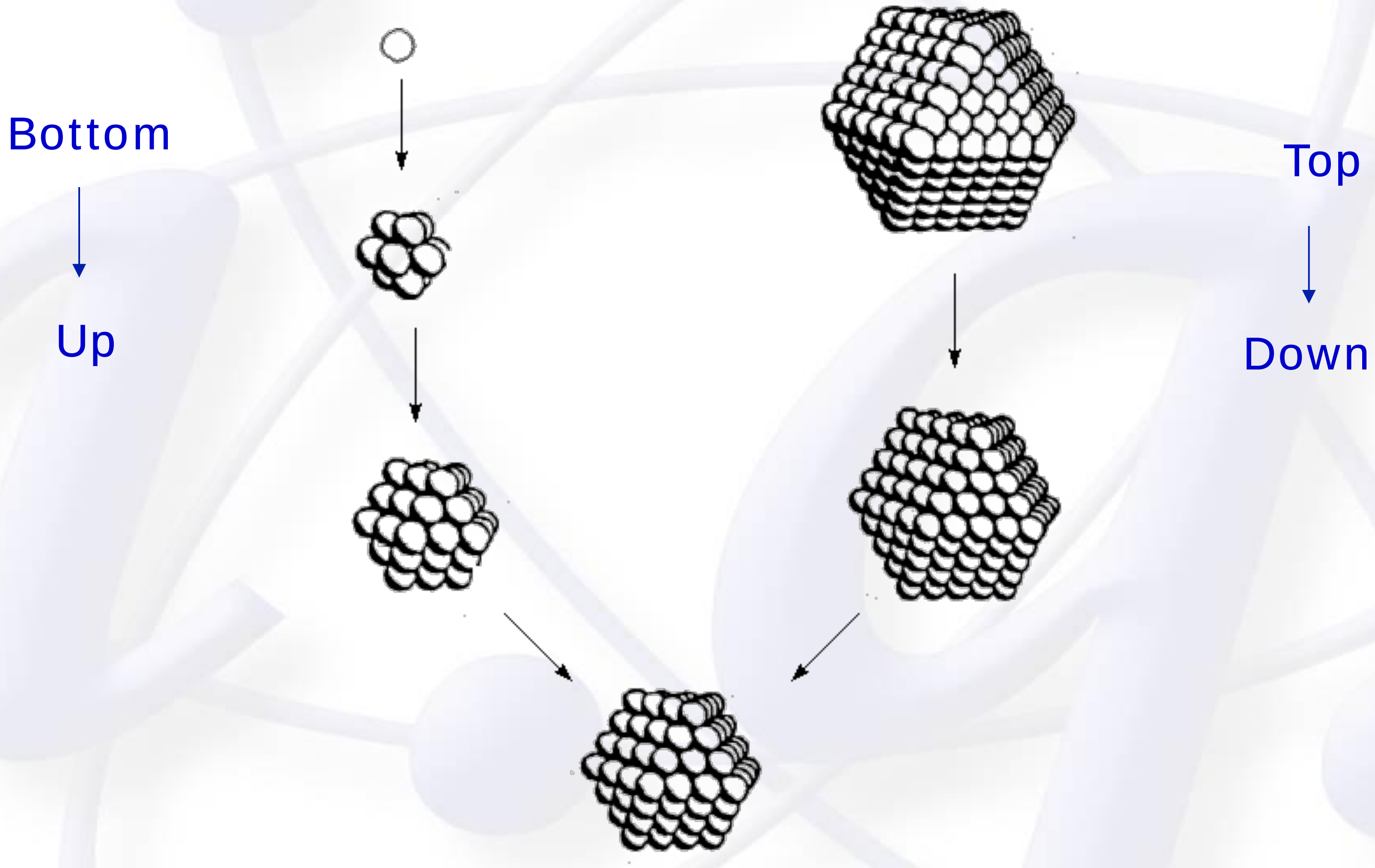
Org. Lett. **2008**, *10*, 237.





Adv. Synth. Catal. **2008**, *350*, 160

Preparation of the transition-metal nanoparticles



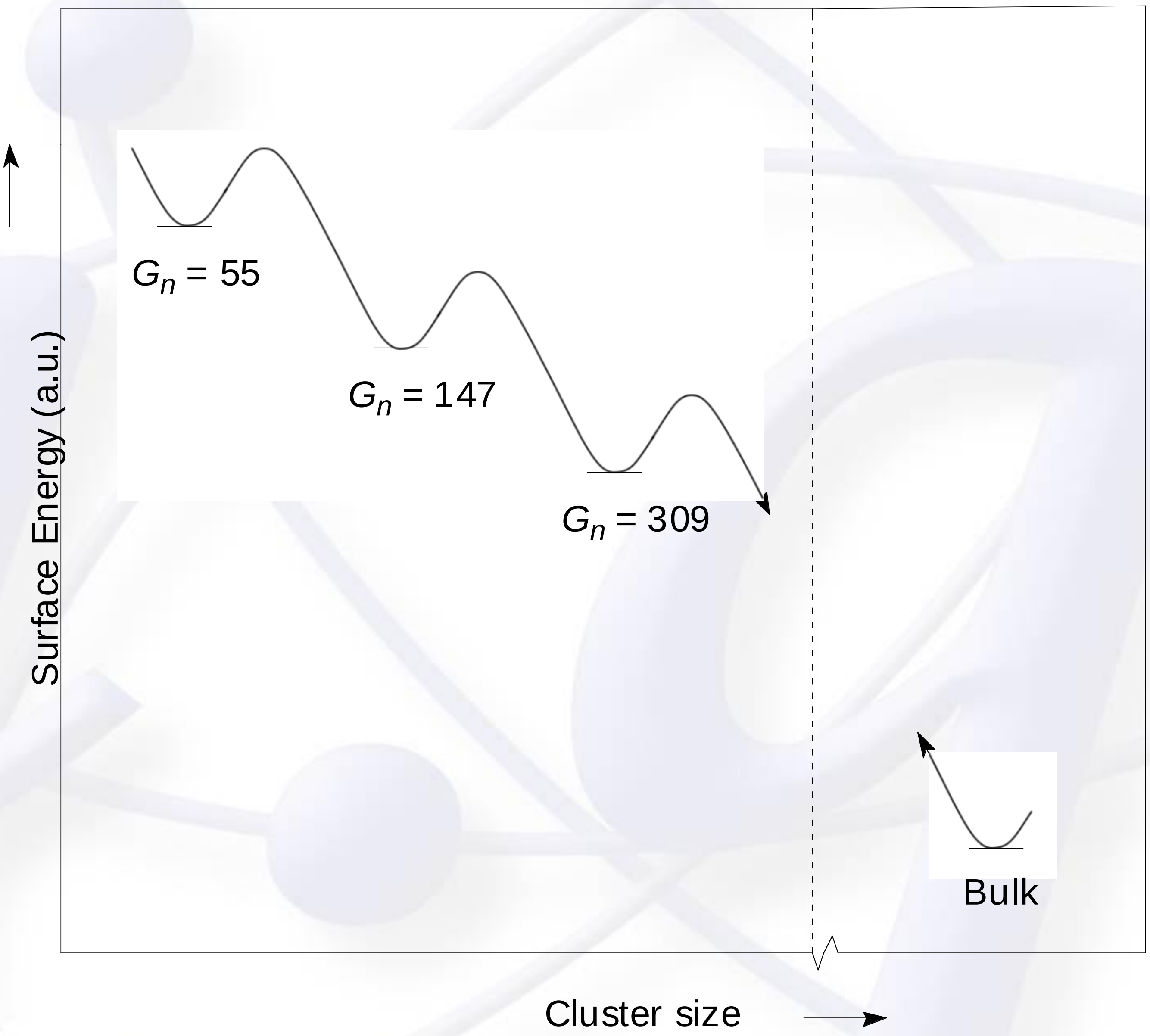
“Magic Numbers” of Transition-Metal Nanoparticles

Full-Shell "Magic Number" Clusters

Number of shells	1	2	3	4	5
Number of atoms in cluster	M_{13}	M_{55}	M_{147}	M_{309}	M_{561}
Percentage surface atoms	92%	76%	63%	52%	45%

Idealized representation of hexagonal close-packed full-shell ‘magic number’ clusters. Each metal atom has the maximum number of nearest neighbors, which imparts some degree of extra stability to full-shell clusters.

Surface Energy



Transition-metal nanoclusters are only kinetically stable

Stabilization

Electrostatic | Steric

- Coordination of anionic species (X, CO_2, polyoxoanions, ...)
- Polymers, dendrimers, alkylammonium cations, ...

R. G. Finke in *Transition-Metal Nanoclusters* (Eds. D. L. Feldheim, C. A. Foss Jr.) Marcel Dekker, New York, **2002**, Chapter 2, pp. 17-54

BMI.PF_6

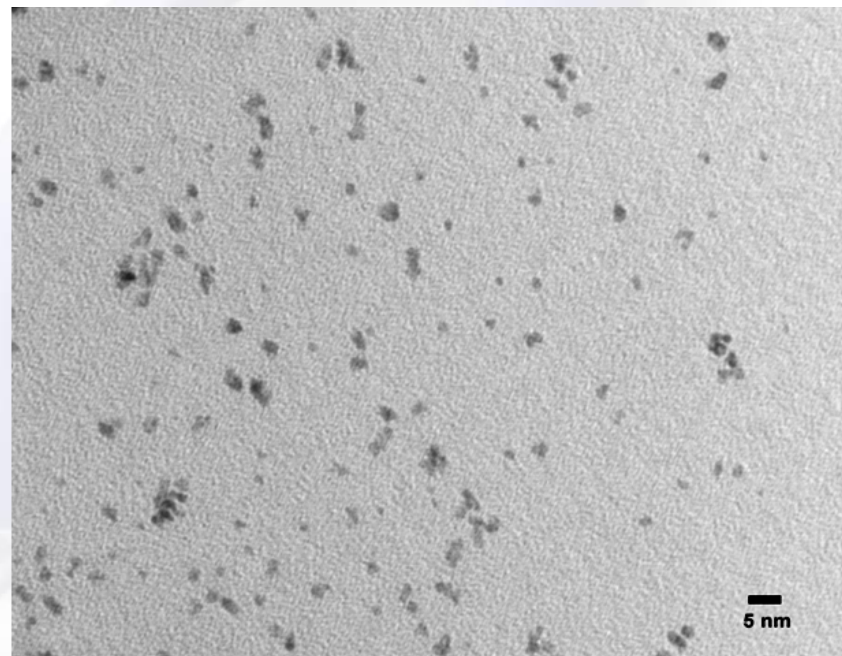
H_2 (4 atm), 75ºC
25 min

[Ir(cod)Cl]$_2$

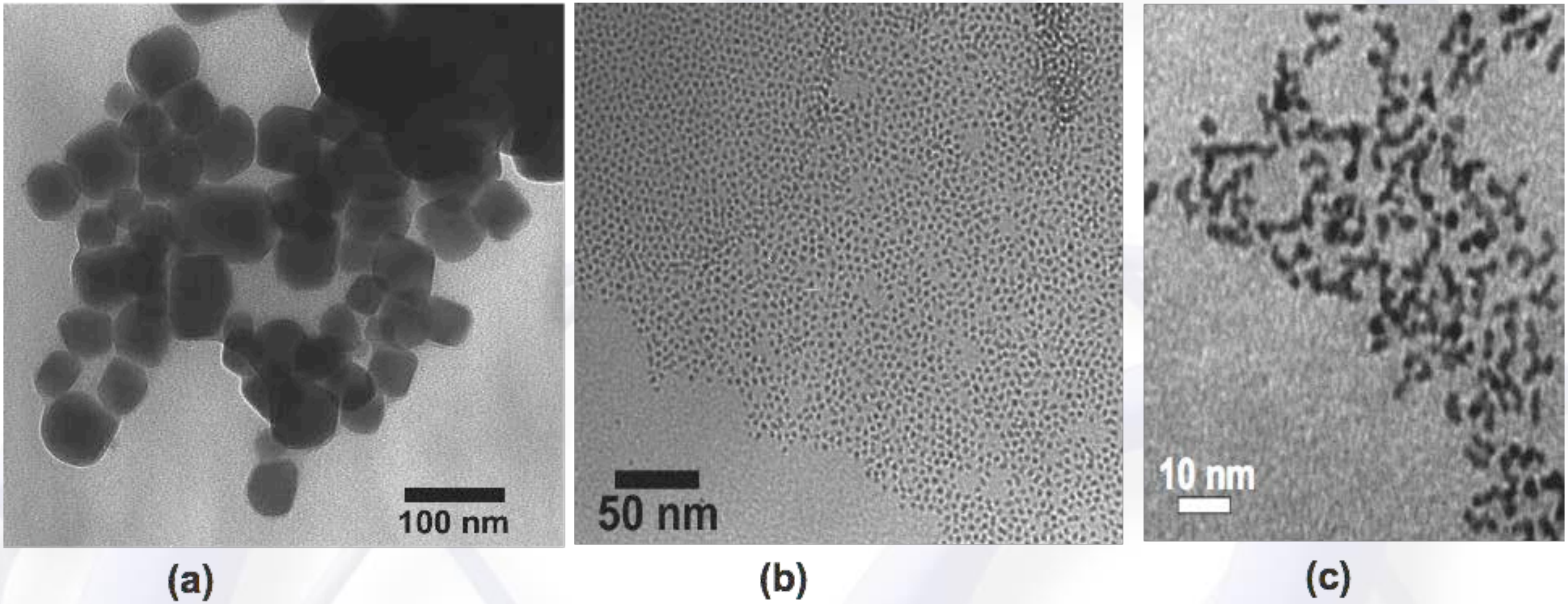
[Ir(0)]$_n$ dispersed

in BMI.PF_6

(2.3 ± 0.3 nm)



J. Am. Chem. Soc. **2002**, *124*, 4228;
Revue: *Chem. Eur. J.* **2007,** *13*, 32.

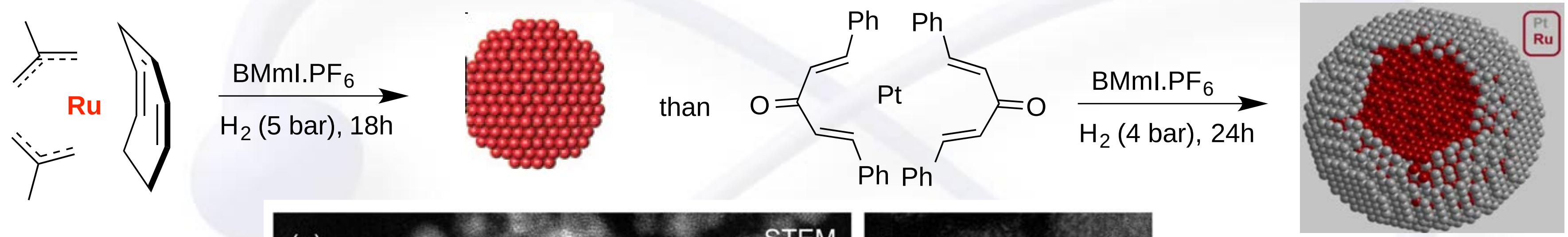


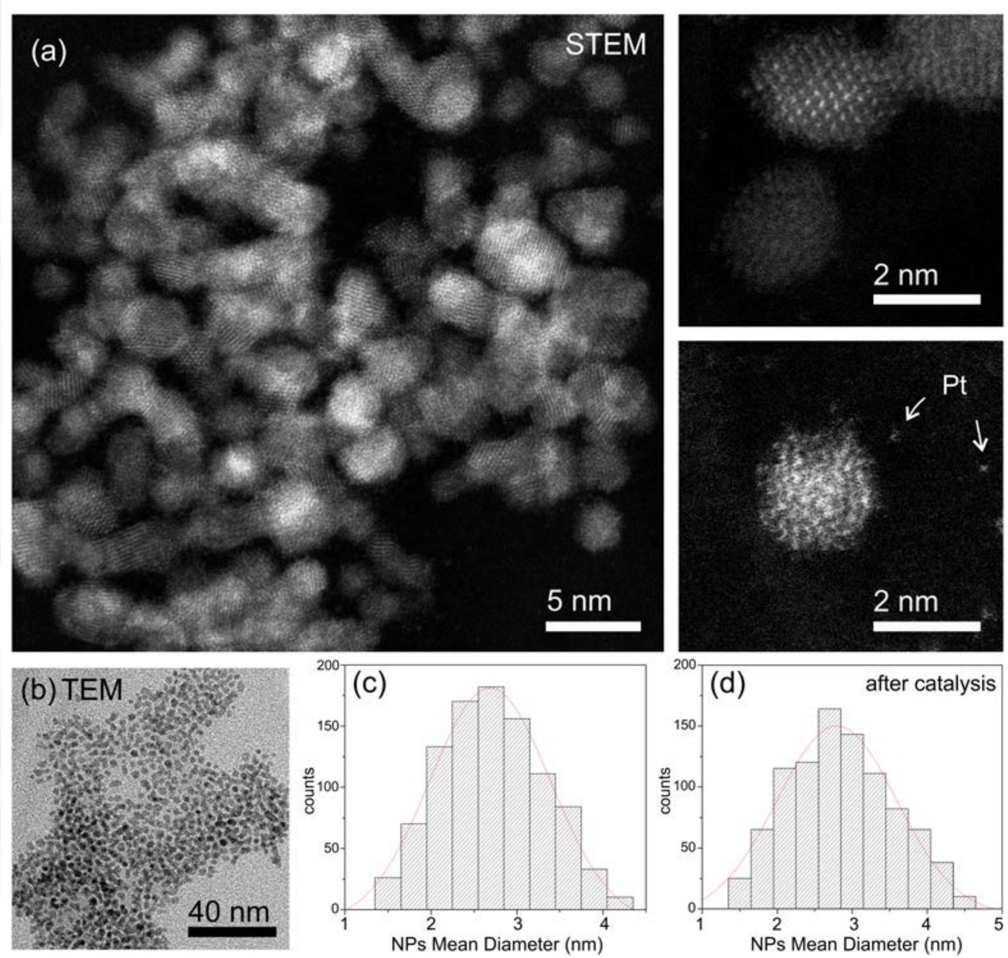
Examples of nanostructures prepared and characterized in imidazolium ionic liquids (*in situ TEM micrographs): a) Co(0) nanocubes; b) spherical Ru(0) nanoparticles and c) worm-like Ir(0) nanoparticles.*

Angew. Chem. Int. Ed. **2008**, *47,* 9075.

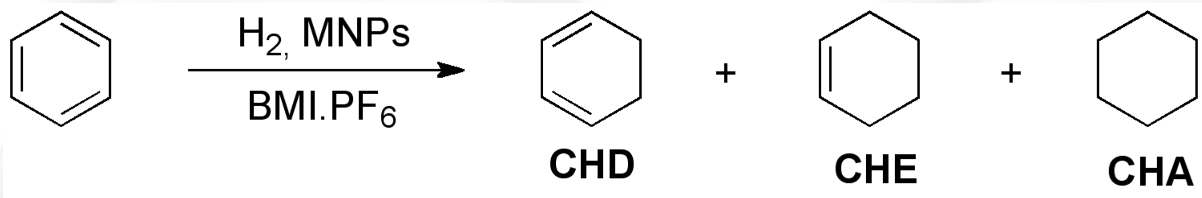
Inorg. Chem. **2008**, *47,* 8995.

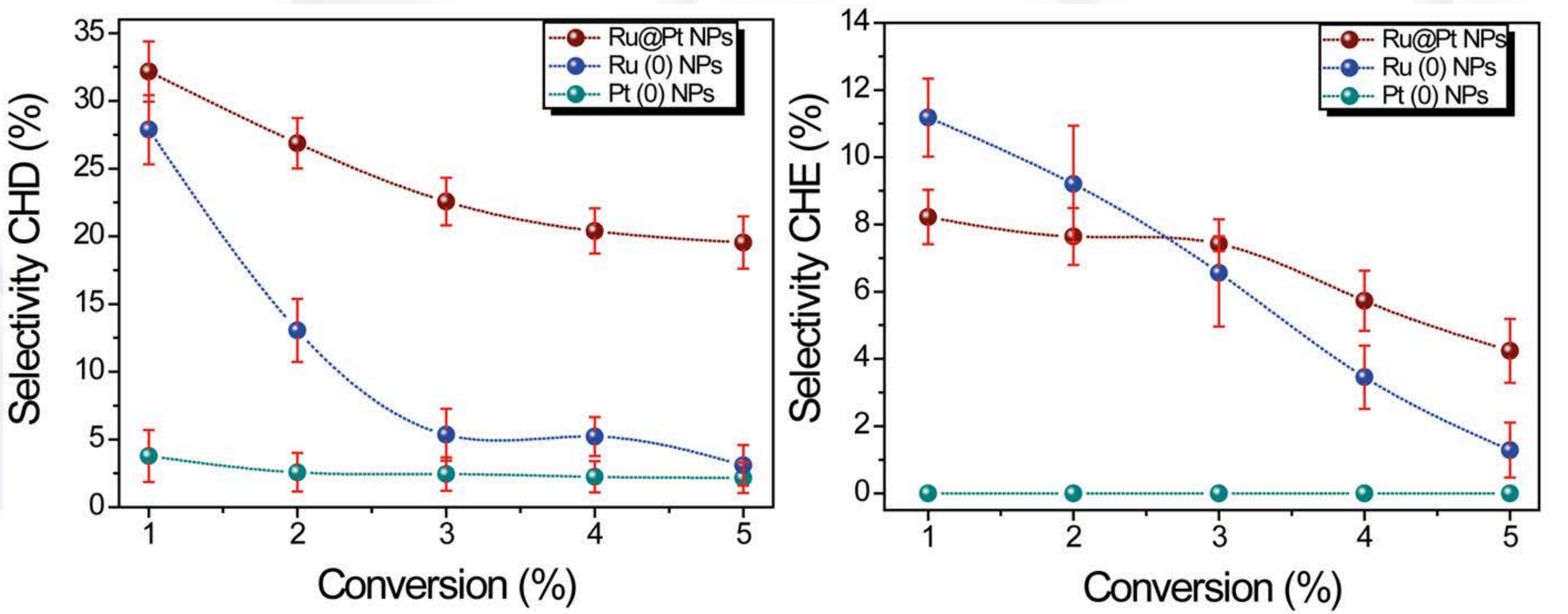
P. Migowski 2009 MsC Dissertation





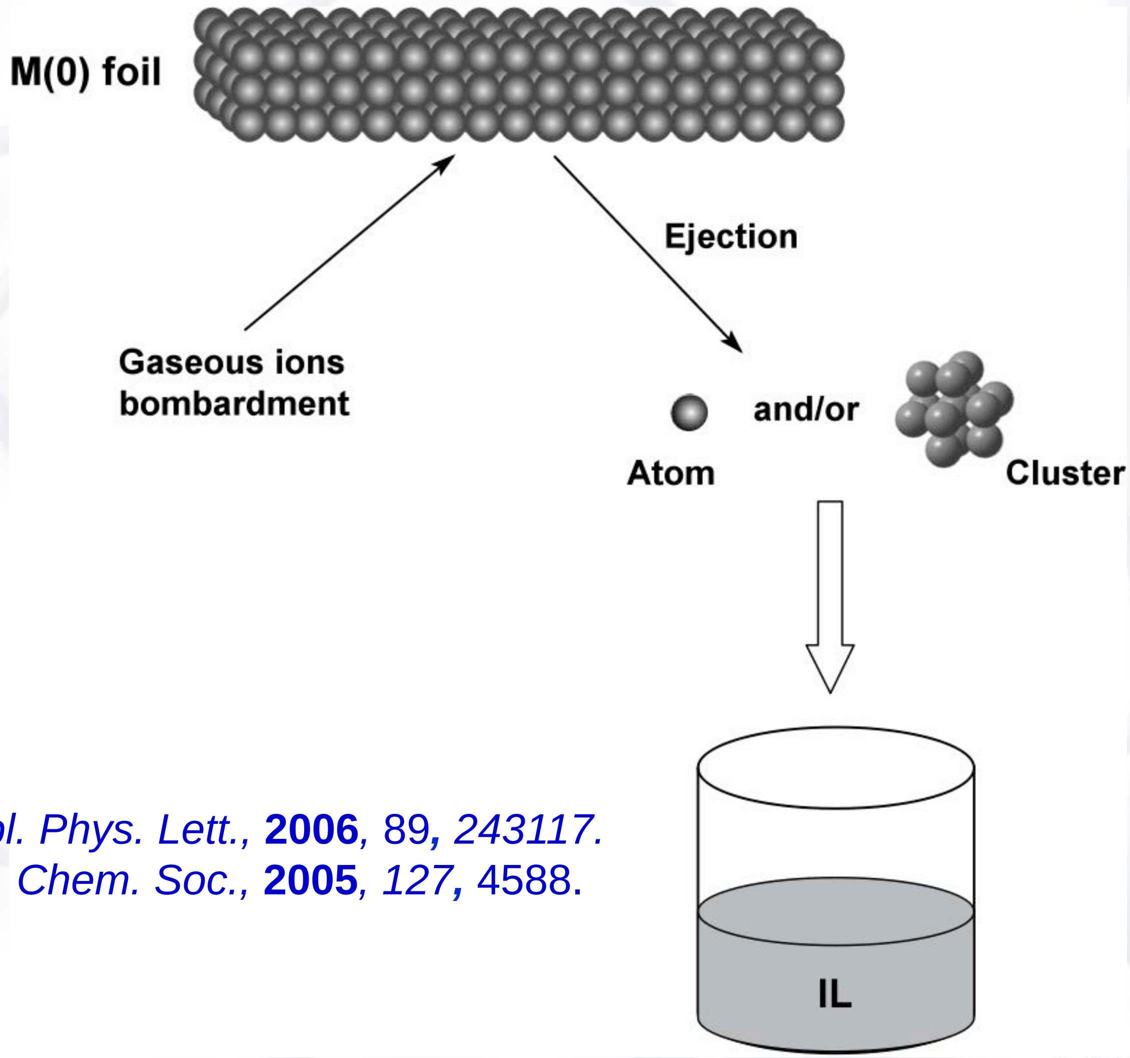
Micrographs of the Ru@Pt NPs in BMI.PF_6; (a) HAADF-STEM (300 kV); (b) TEM (120 kV); size distribution histogram (c) before and (d) after catalysis. HAADF-STEM images of isolated Ru@Pt NPs are shown at insets



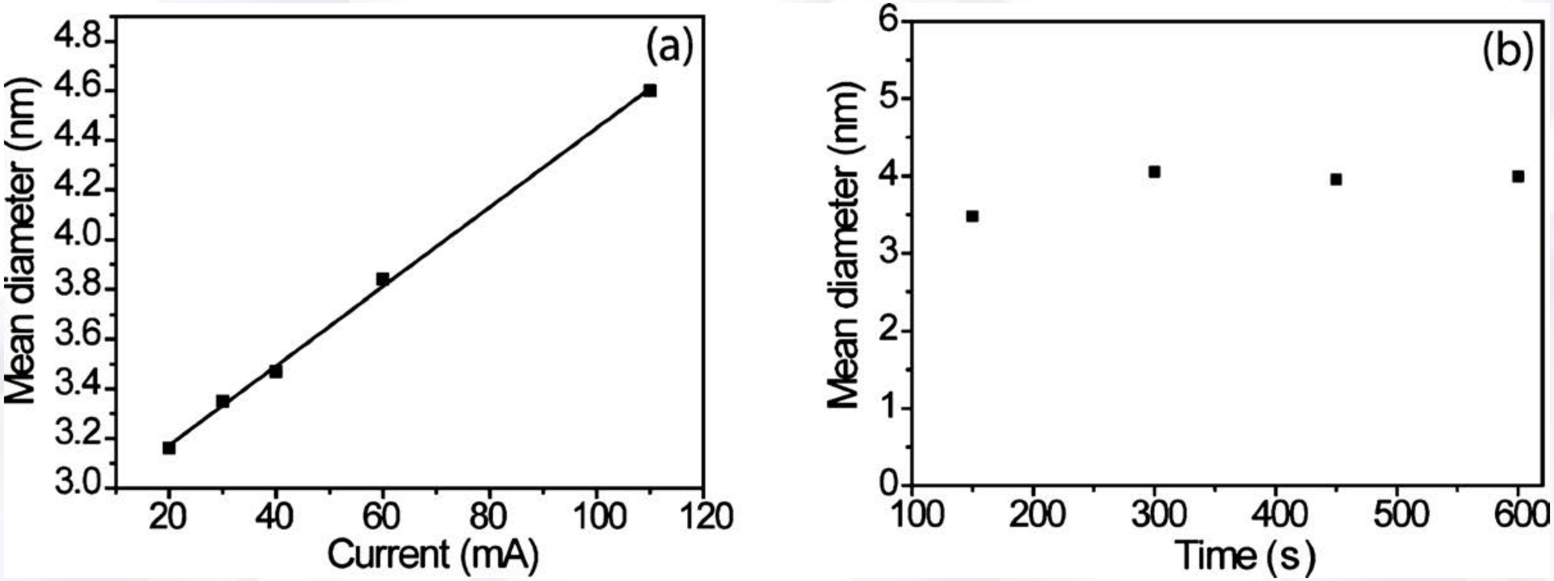


Selectivity of the partial hydrogenation products ((a) 1,3-CHD and (b) CHE) vs. benzene conversion. Reaction conditions: 0.77 µmol metal NPs, benzene/metal (mol ratio) = 730, 1 mL BMI.PF_6, 60 °C and 6 bar of H_2. Co-solvent: 4 mL *n*-heptane. Conversion and selectivity determined by GC and GC-MS

Metal Nanoparticles Deposition in ILs by Bombardment

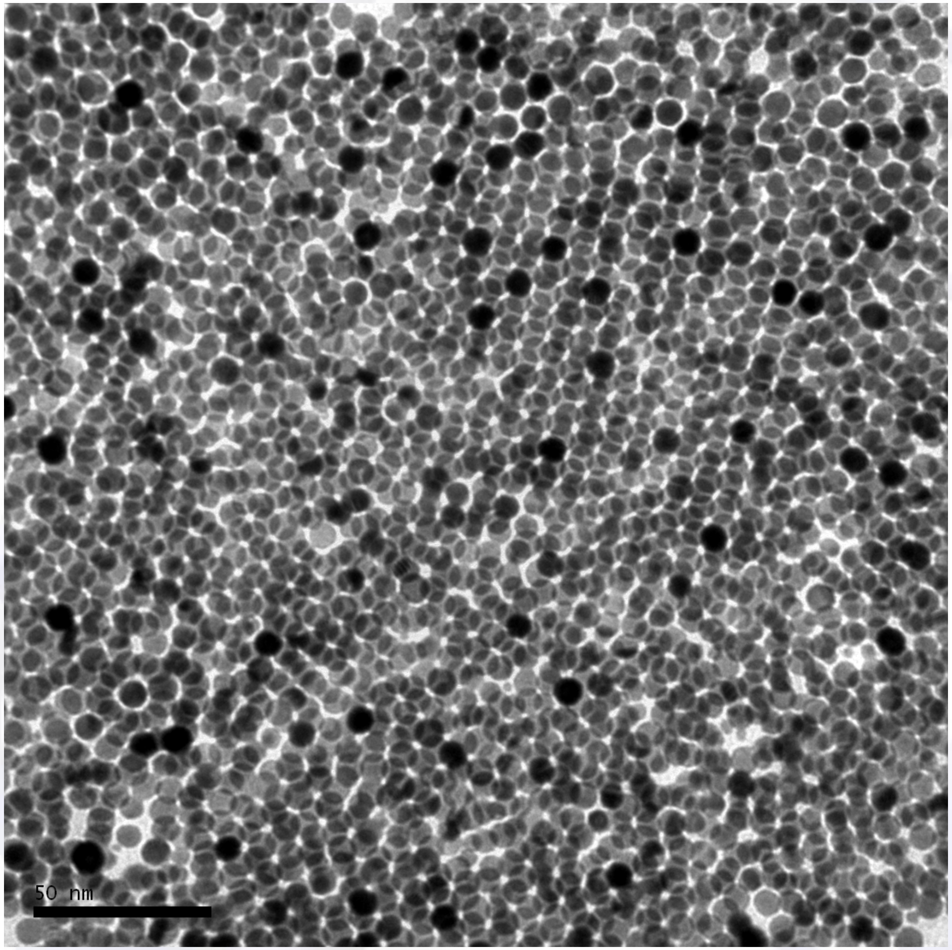


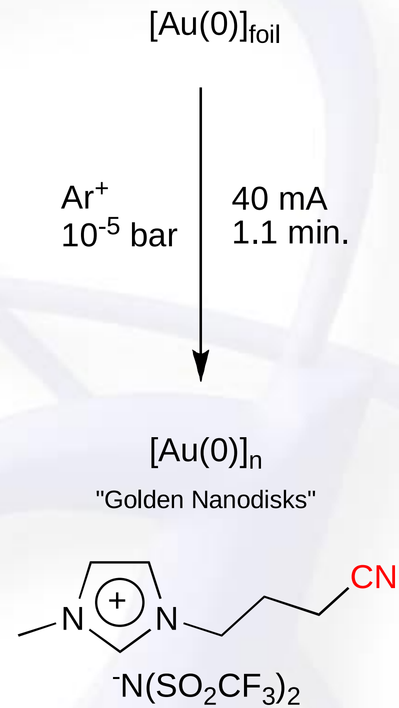
(Ar+) T. Torimoto et al. *Appl. Phys. Lett.*, **2006**, 89**,** *243117.*
(*h*ν) J. Dupont et al. *J. Am. Chem. Soc.*, **2005**, *127***,** 4588.

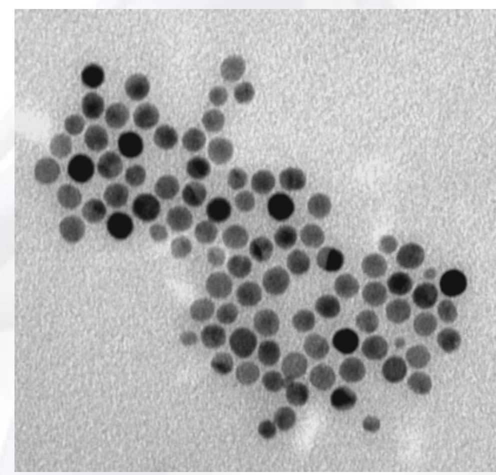


(a) Mean diameter of Au NPs obtained in BMI.NTf2 after 150 s of deposition using different discharge currents; (b) diameter versus deposition time for Au NPs obtained in BMI.NTf2 at a fixed sputtering current of 40 mA (325 V). (Adapted with permission from ref 74. Copyright 2010 American Chemical Society.)

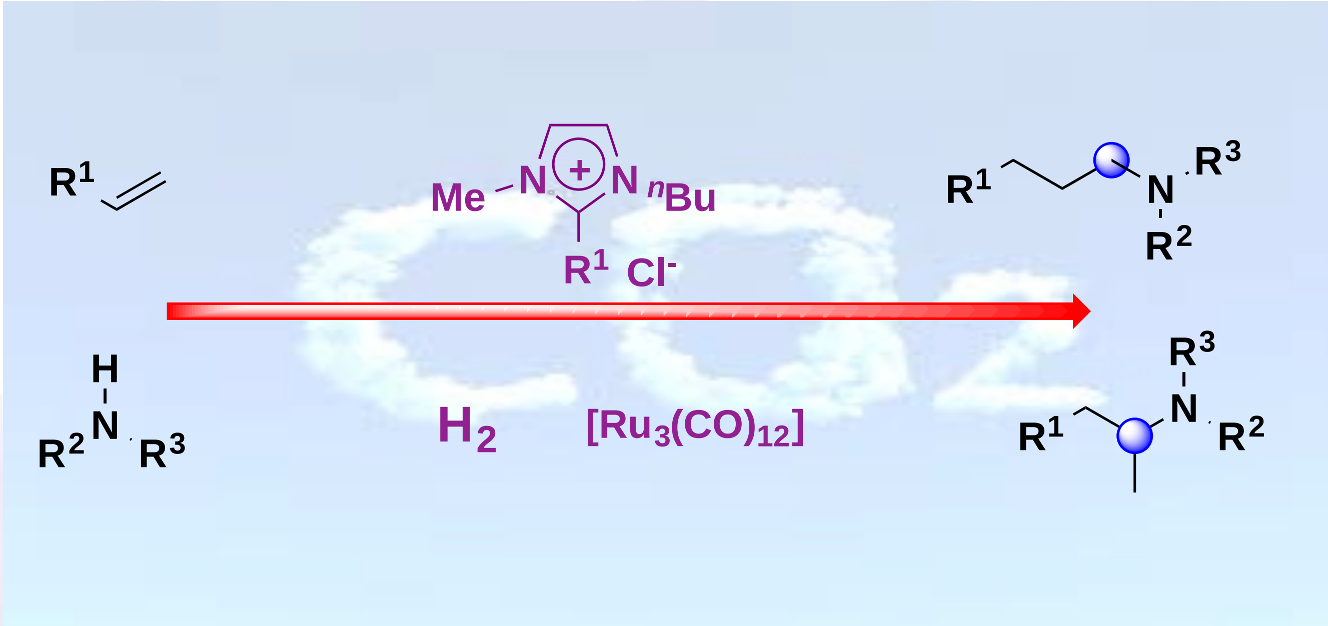
Acc. Chem. Res. **2011,** 44, 1223-1231.

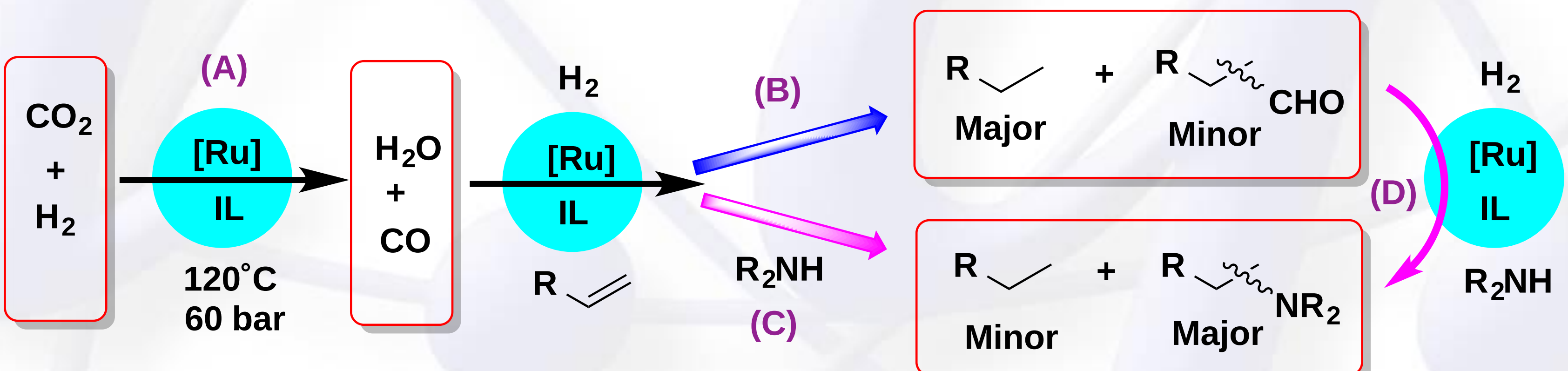






Golden “nanodisks”





ChemSusChem, **2016**, DOI: 10.1002/cssc.201600385

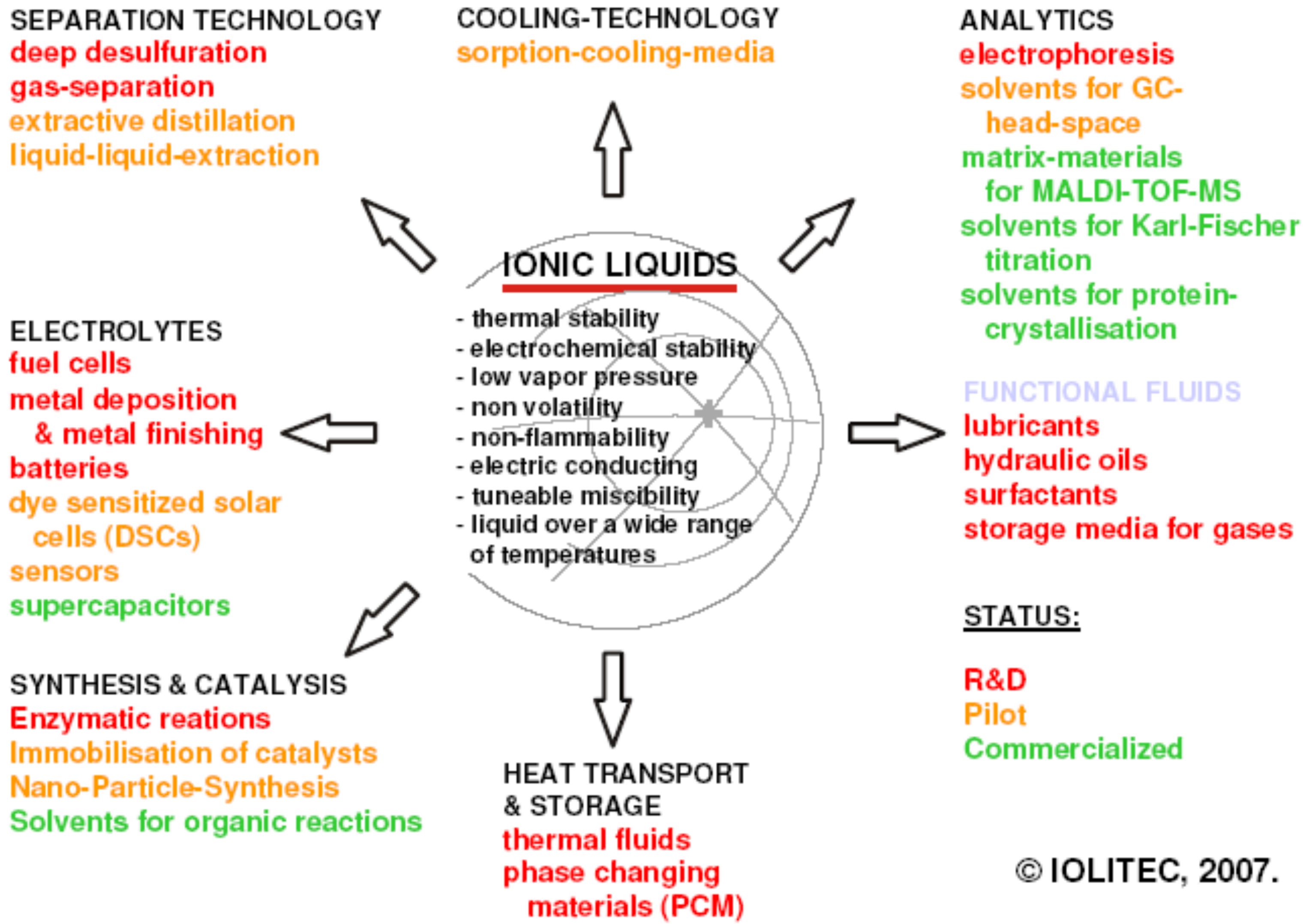


Figure 1. Potential application fields of ionic liquids including their commercialisation status.

BR
PETROBRAS

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

Ciência e Tecnologia
Ministério da Ciência e Tecnologia

CAPES

i.q.

UFRGS

inct
institutos nacionais de ciência e tecnologia

Alexander von Humboldt
Stiftung / Foundation

twas

MERCK

Fapergs

i.q.
UFRGS

IL - Nano

Dr. Giovanna Machado
Dr. A. Lapis
Marcos A Gelesky (PhD)
Claudia C Cassol (PhD)
Marcelo P. Stracke (PhD)
Bauer Ferreira (PhD)
Sandra X. Chiaro (PhD)
Jackson D. Stocken (PhD)
Pedro M. da Silva (MsC)
Fabricio Flores (MsC)

P. Fichtner – UFRGS (TEM)
S. R. Texeira – UFRGS (XRD)
J. Morais – UFRGS (XPS)
W. Loh (UNICAMP)
M. Eberlin (UNICAMP)
F. Rominger (Heidelberg)

Palladacycles

Dr. Gunter Ebeling
Dr. Brenno A. Silveira
Gilbert Rosa (MsC)
Fabiana S. Mancilha (MsC)
Aline S. Lopes (MsC)
Vinicius Reis (UG)

Ex

Paulo A Z Suarez (UnB)
Silvana Silva (CSI-Porto Alegre)
Alexandre P Umpierre (Lyon)
Crestina S Consorti (Erlangen)
Glédison S. Fonseca (BASF, Germany)
Carla W Sheeren (Strasbourg)
Edson T Silveira (UERS)
Liane M Rossi (USP-SP)