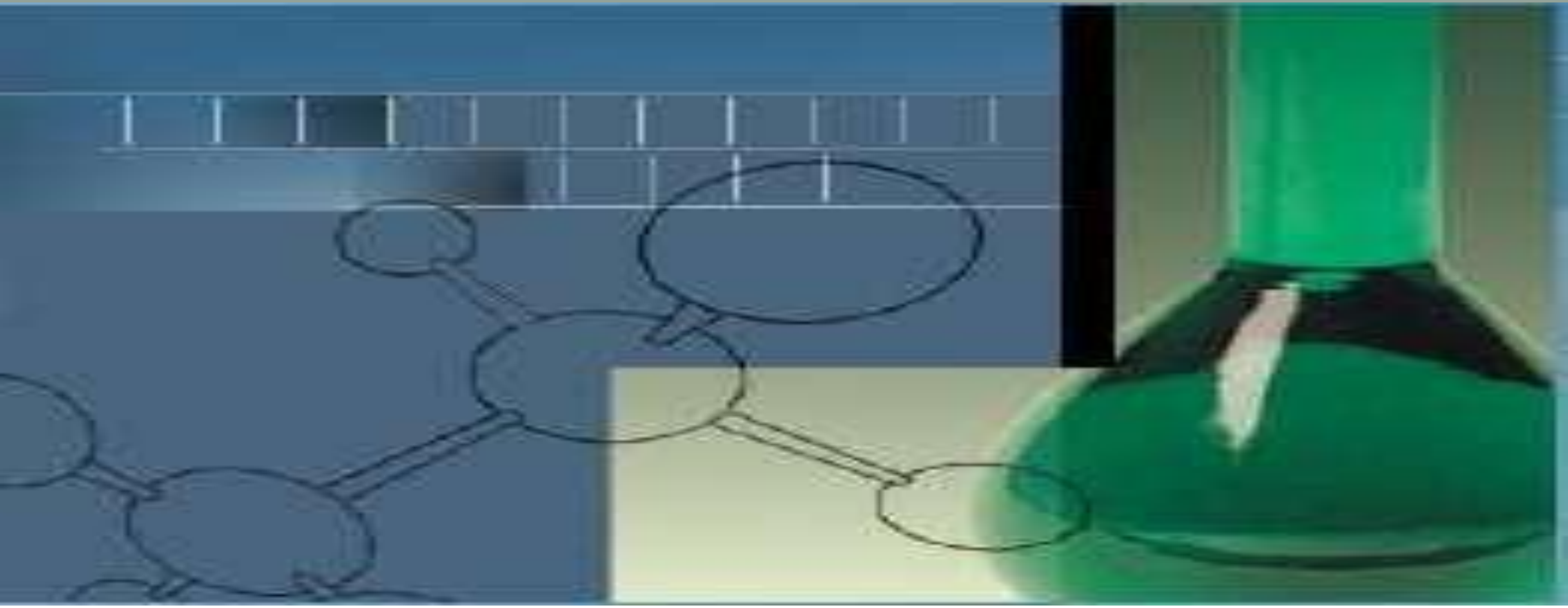
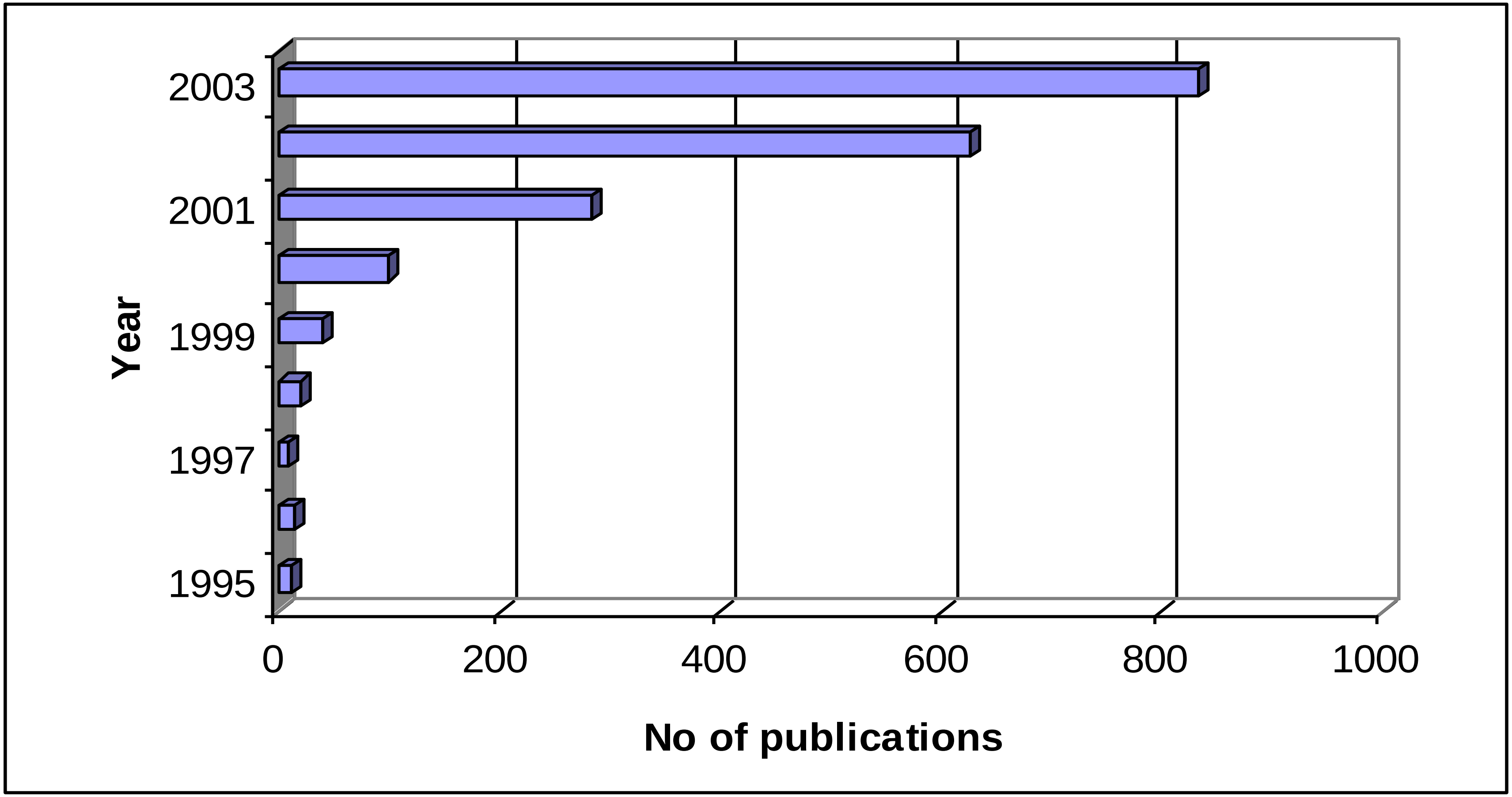


Ionic Liquids:

Green Solvents For The Future

Development



Outline

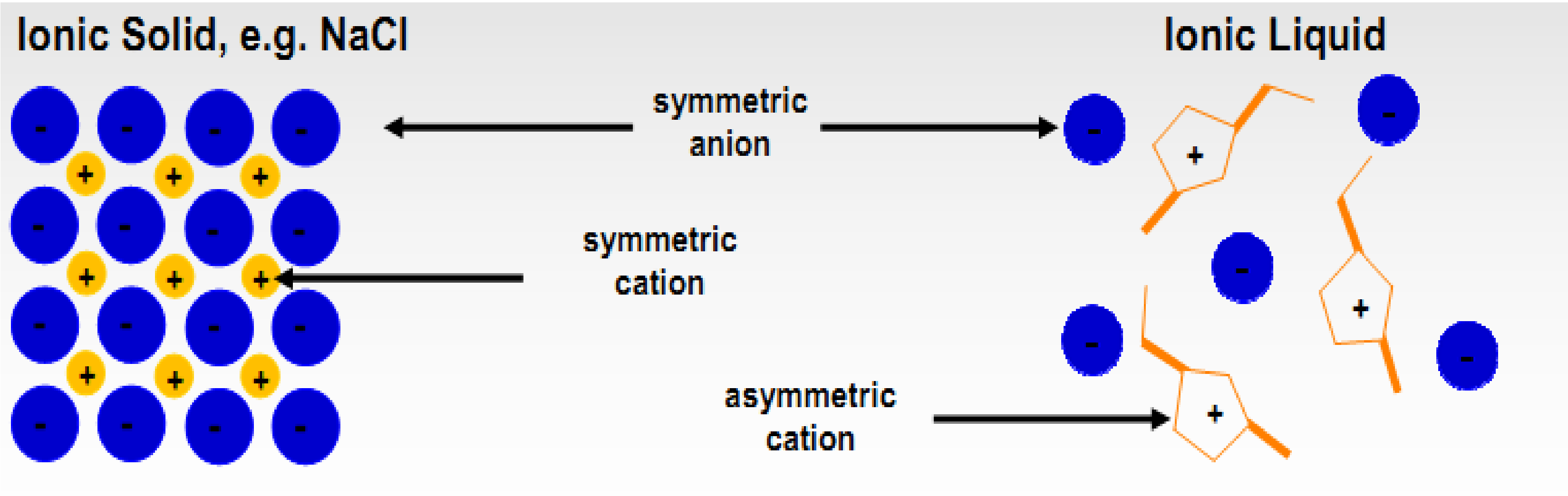
- Definition
- Advantage
- Applications
- Ionic liquid in synthesis
- Examples
- Conclusion

What are Ionic Liquids

Common Definition

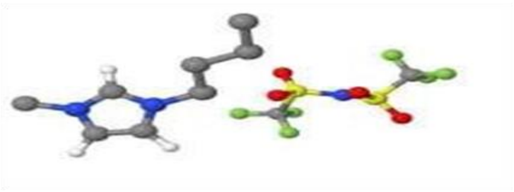
- Ionic Liquids (ILs) is the generic term for a class of materials, consisting entirely of ions and being liquid below 100° C.

- If they are liquid at room temperature, we call them room temperature ionic liquids (RTILs).



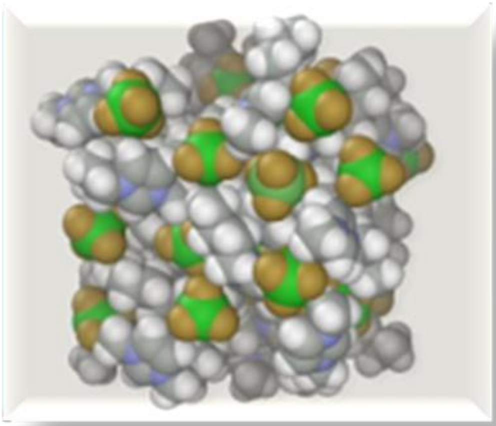
H_2O

Organic solvents

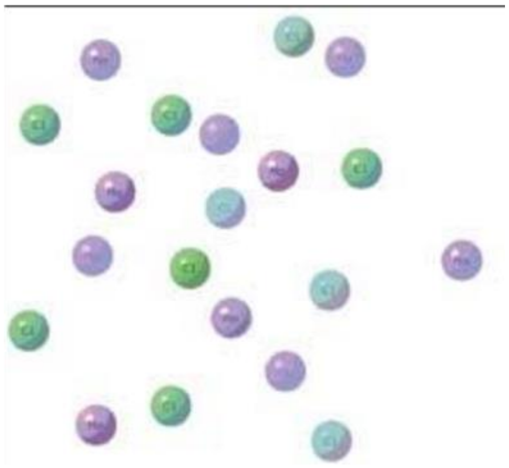


Ionic Liquids

Why are ionic liquids “liquids

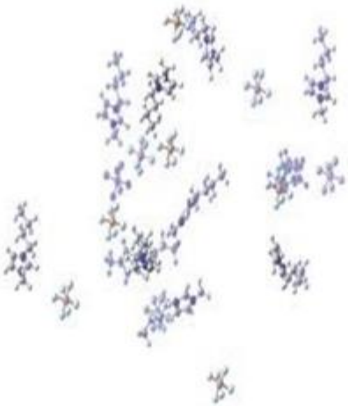


A simulated model of
an Ionic Liquid



liquid NaCl

molten BMIM PF6



aqueous NaCl

Examples of common Ionic Liquids:

- **Ethyl-3-methylimidazolium (EMIM) Chloride,**
- **EMIM dicyanamide,**
- **1-butyl-3,5-dimethylpyridinium bromide,**
- **1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6]**

  * $[PF_6]^-$ for moisture stable, water immiscible IL

  * $[BF_4]^-$ for moisture stable, but water miscible IL

  * $[AlCl_4]^-$ (or other Lewis acids) decomposes in water

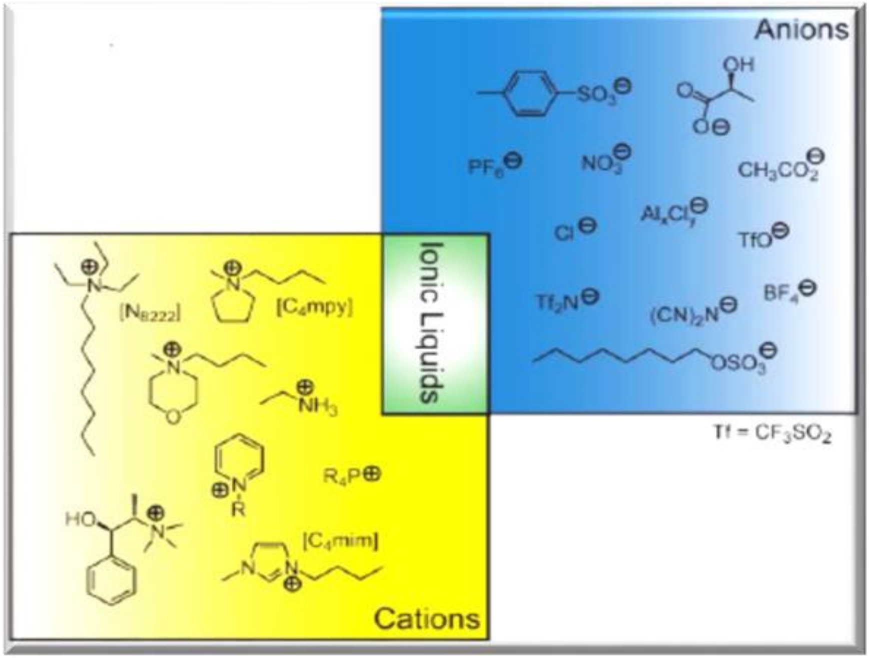


Fig: Some common cations and anions in Ionic Liquids

Designers solvent – ionic liquids

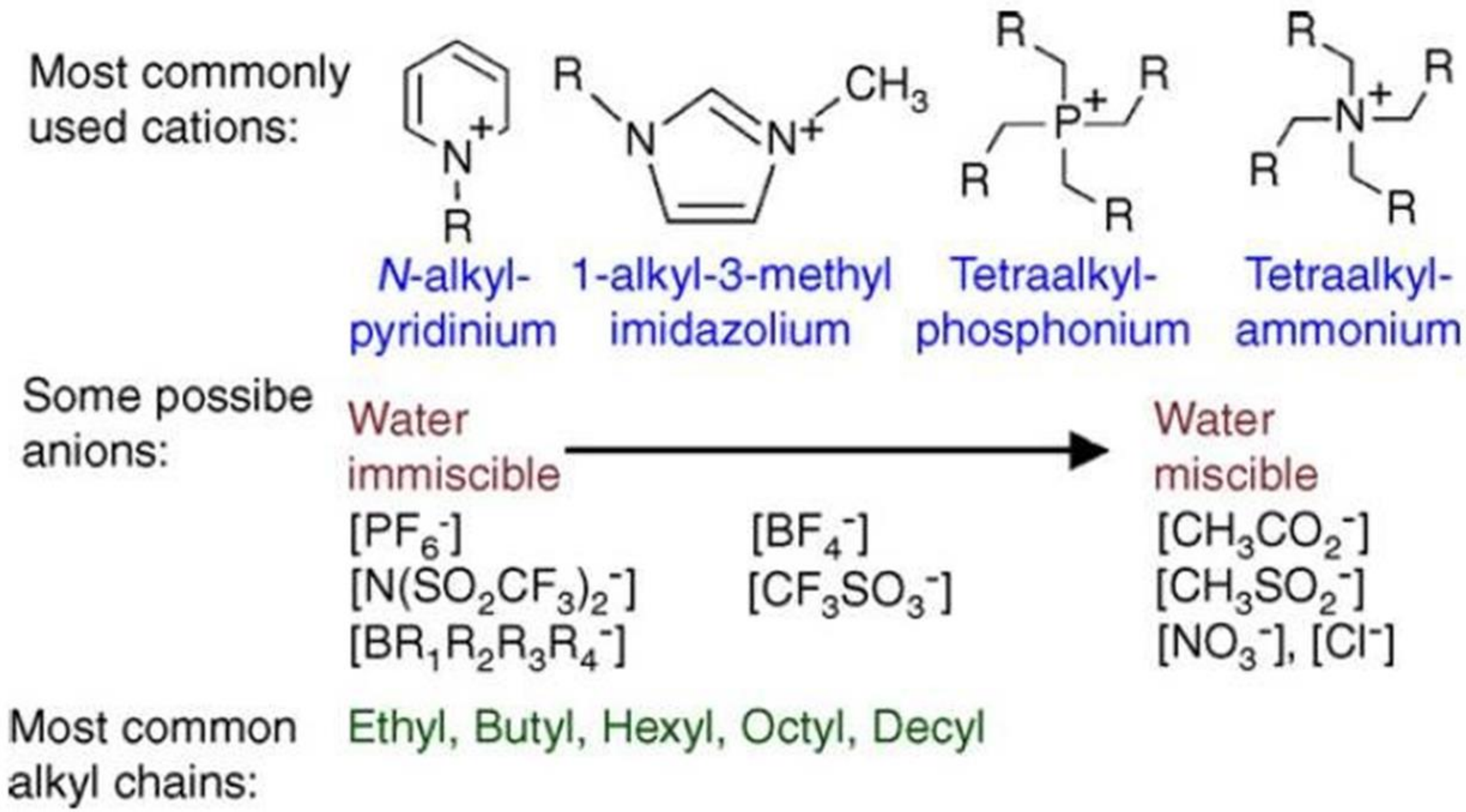
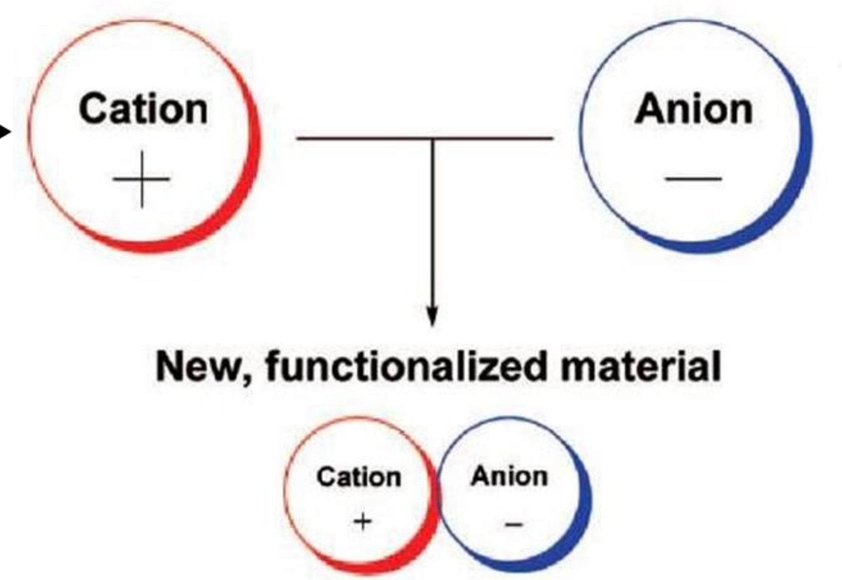


Fig. 3. Most commonly used cation structures and possible anion types [50]

Designers solvent – ionic liquids

1.Viscosity
2.Surface tension
3.Melting point



1.Oxygen balance
2.Density
3.High energy content ion

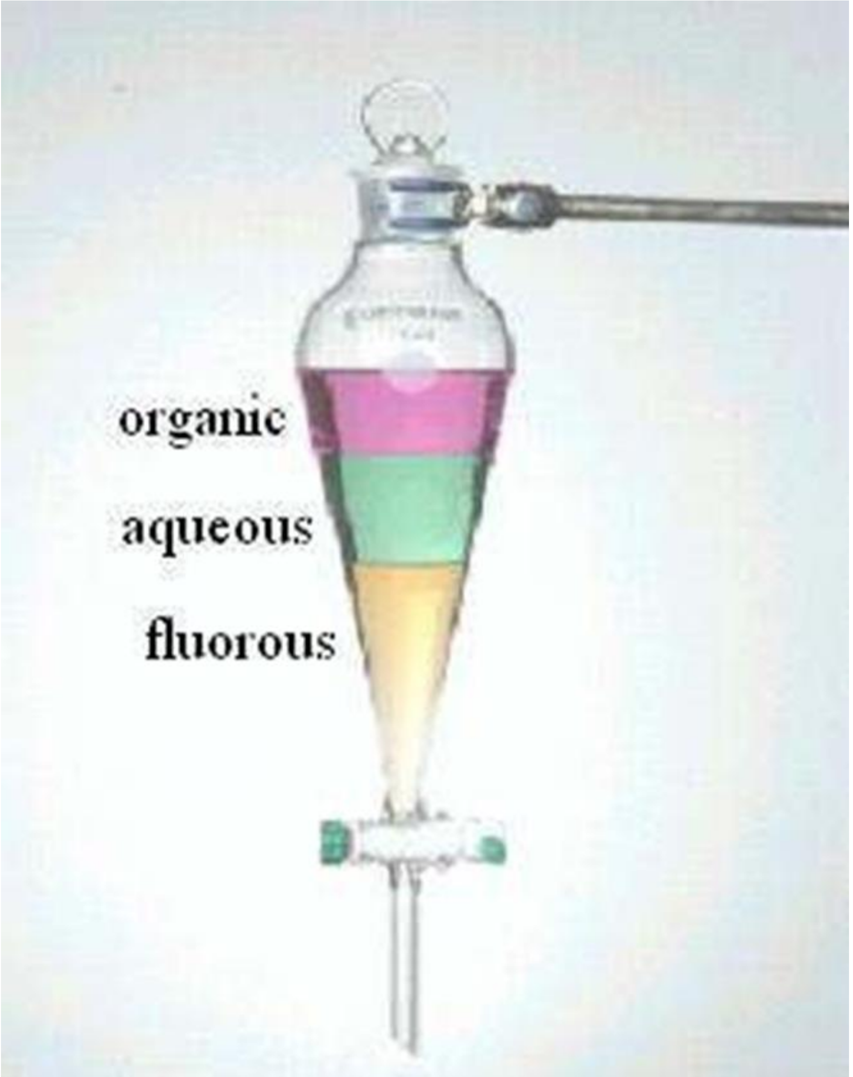
Functionality

Stability

About 1000 ILs are described in the literature, 300 are commercially available.

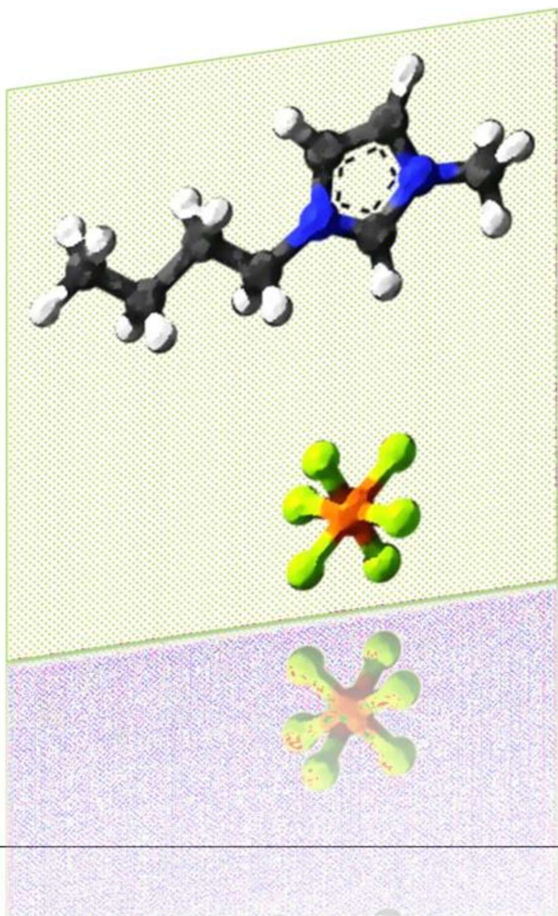
$[BF_4]^-$ $[PF_6]^-$ $[NTf_2]^-$

Fluorous ILs are immiscible with both organic and aqueous solvents.

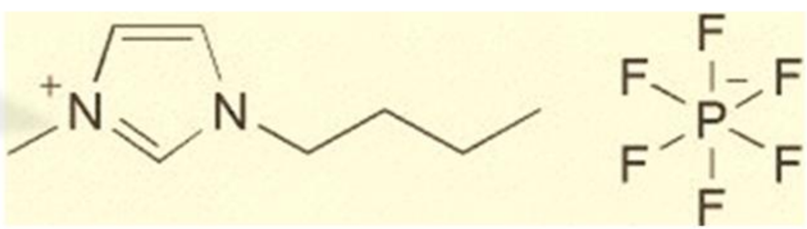


[BMIM][PF_6]

1-Butyl-3-methylimidazolium hexafluorophosphate



- A viscous, colourles, hydrophobic and non-water soluble ionic liquid.
- Molecular mass:284.18 g mol−1
- Density: 1.38 g/mL
- Melting Point:10˚C



Paul Walden

Discovery and History

- **Era of ionic liquids -began in the eighteen hundreds- Gabriel & Weiner reported an ionic liquid**
- **First ionic liquid: ethyl ammonium nitrate (1914, Paul Walden)**

*** The first room temperature ionic liquid -1951**

- **N-ethylpyridinium bromide- aluminium chloride melt**

*** The most stable and conductive salts - 1982**

- **1,3-dialkylimidazolium salts**

*** The hydrophobic ionic liquids - 1992**

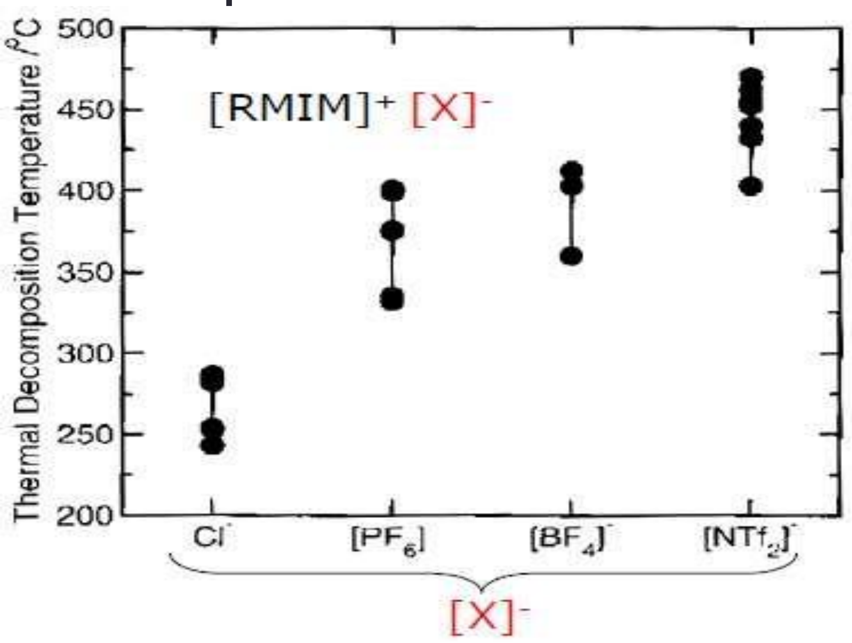
- **1-ethyl-3-methylimidazolium tetrafluoroborate**

SALIENT FEATURES

- Vapour Pressure
- Melting Point
- Viscosity
- Miscibility with water
- Thermal Decomposition

Vapour Pressure of Ionic Liquids

- They have small or negligible vapour pressure
- Higher thermal decomposition point
- Ecological Solvents
- Unique solvent



Melting Points of ILs

- Large range of temperature (-900C to 1500C)

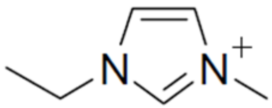
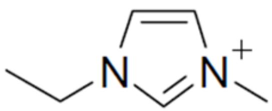
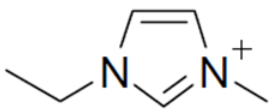
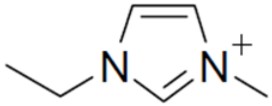
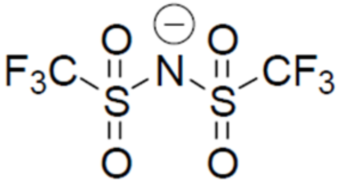
- Modulation of melting point with variation of anion &/or cation size.

Generally :

size of cation or/and anion increases → melting point decreases

Examples :

[EMIM] [X]	$[NR_4]$ [Br]
X = Cl^- ; mp = 87°C	R = Me ; mp > 300°C
X = $[AlCl_4]^-$; mp = 7°C	R = Bu ; mp = 125°C

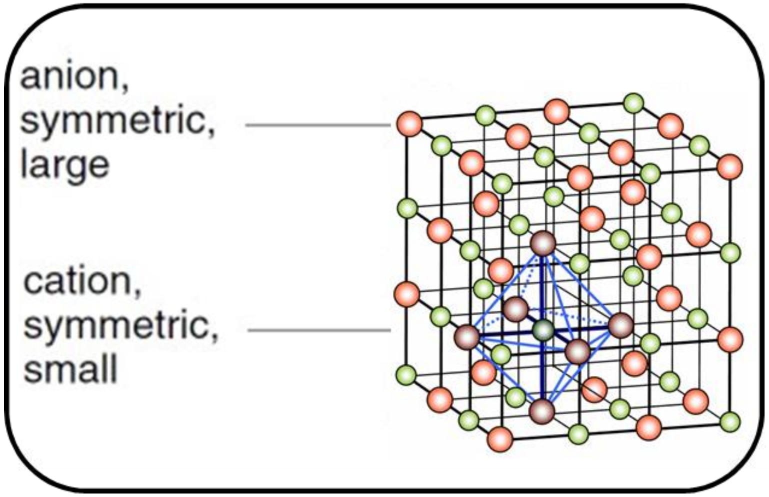
Cation	Anion	T_m / °C
Na^+	Cl^-	801
Cs^+	Cl^-	645
$(Pr)_4N^+$	Cl^-	241
	Cl^-	low 87
	NO_3^-	38
	BF_4^-	15
		–3

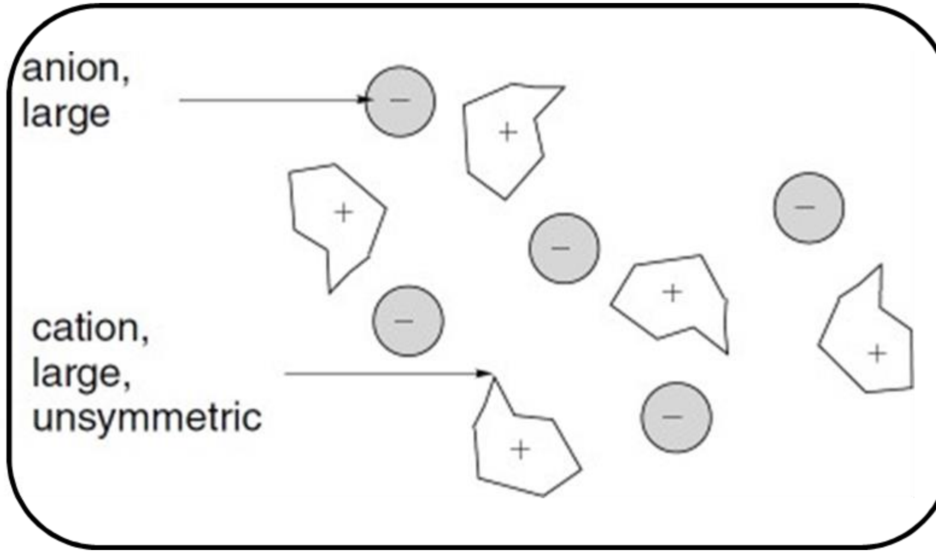
m.p.
high

low

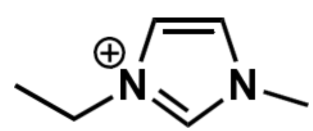
m.p.
cation
and anoin
size
small

large





NaCl



$NTf_2^{\ominus}$

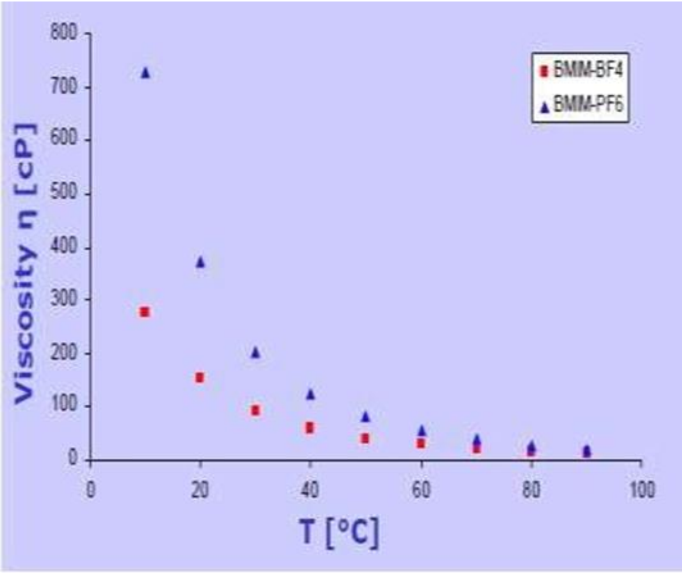
m.p. 801 °C

-3 °C

VISCOSITY OF ILs

- They are usually more viscous than classical solvents

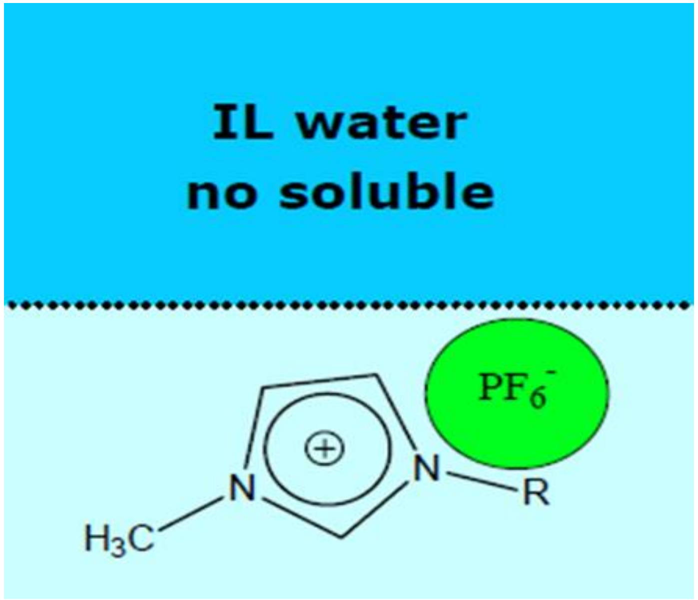
Product	Viscosity [cP] **20°C**
Water	1.0
Toluene	0.6
DMF	0.8
[bmim] [BF_4]	154
[bmim] [PF_6]	371

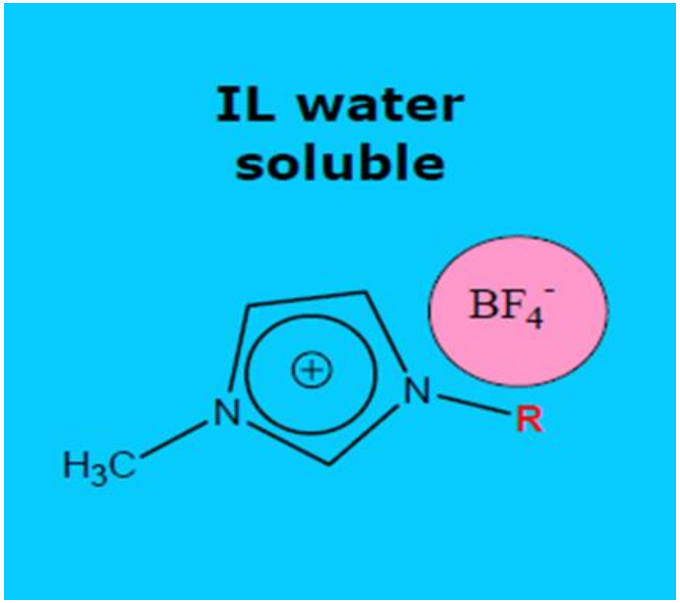


One of the major demerit of ILs

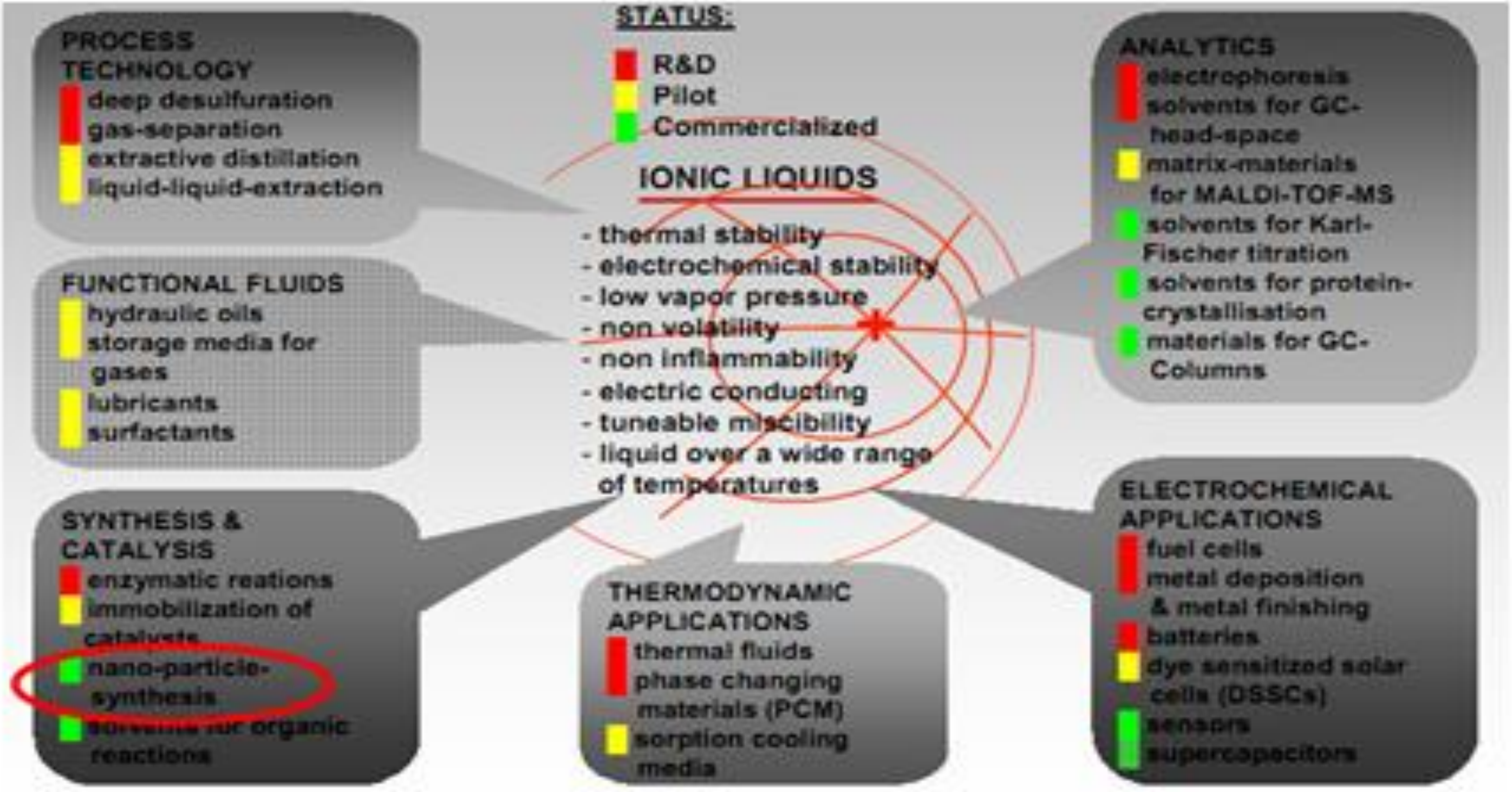
Miscibility with Water

- By changing the nature of ions, It is possible to change miscibility with water

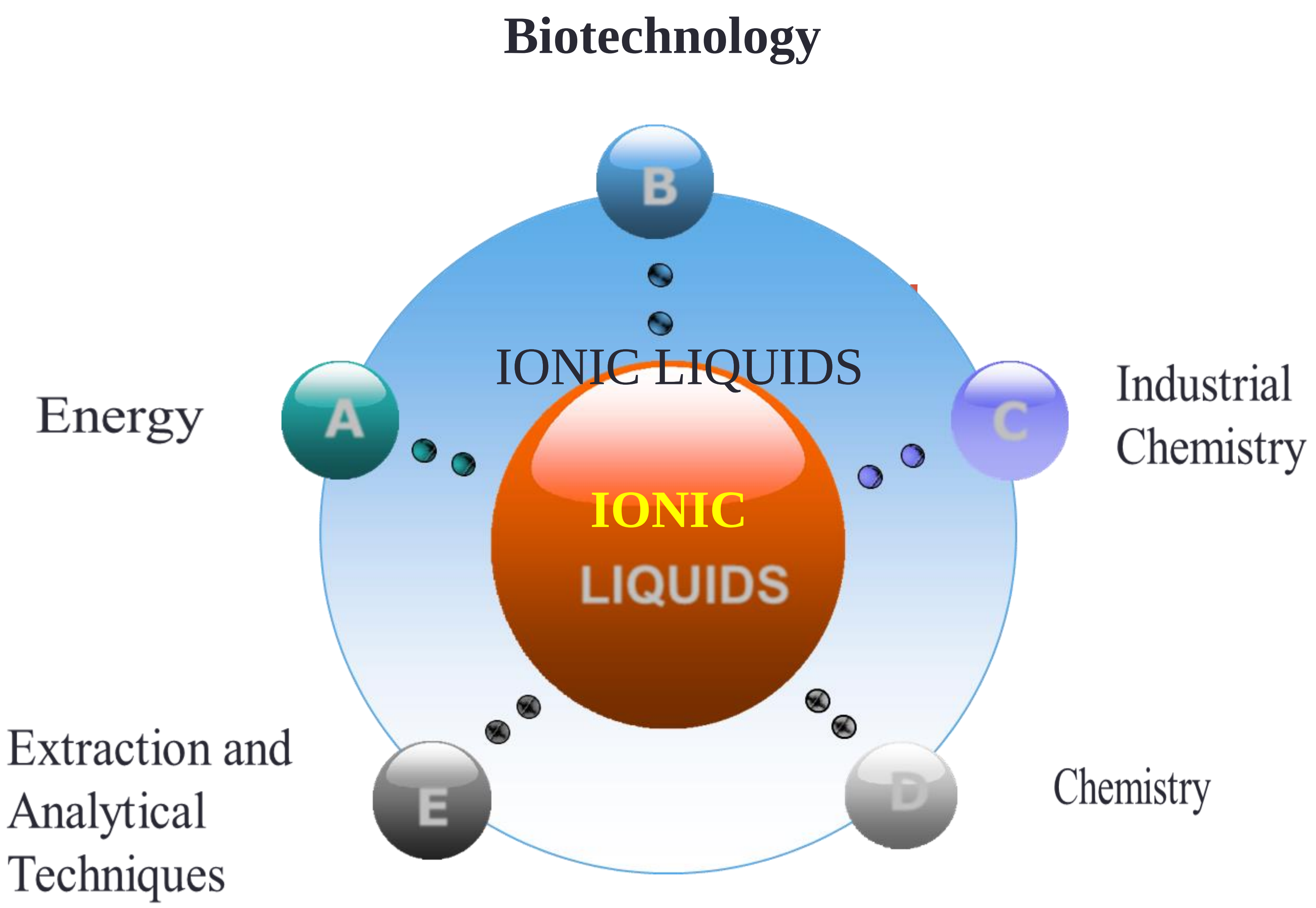




Application



APPLICATIONS



APPLICATIONS

1

BIOTECHNOLOGY

Enzyme catalysis
Protein Synthesis
Cellulose Chemistry

2

ENERGY

Solar Cell
Battery Cell
Heat Storage

3

CHEMISTRY

Heck Reaction
Suzuki Reaction
Diels Alder Reaction
Friedel Crafts Reaction

APPLICATIONS

4

INDUSTRIAL CHEMISTRY

Membrane Separation

5

EXTRACTION

Extraction of Bio-Diesel

6

ANALYTICAL TECHNIQUES

GC Stationary Phase
MALDI

APPLICATIONS

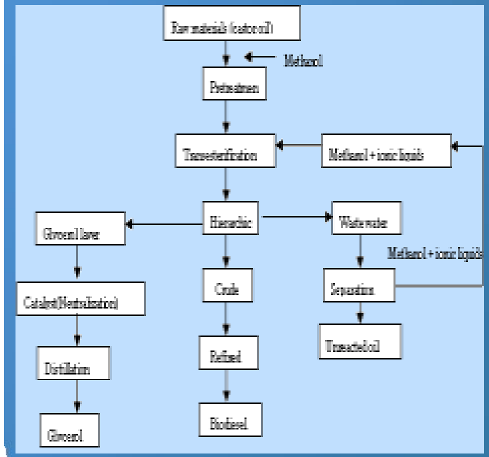
8

CHEMISTRY

Kind of Synthesis	Ionic Liquids
Heck	[bmim] [PF_6]
Suzuki	[bmim] [BF_4]
Keton	[emim] [BF_4]
Diels-Alder	[emim] [Cl]
Aromatic Aldehyde Reduction	[emim] [PF_6]
Friedels-Craft	[emim] [$AlCl_4$]

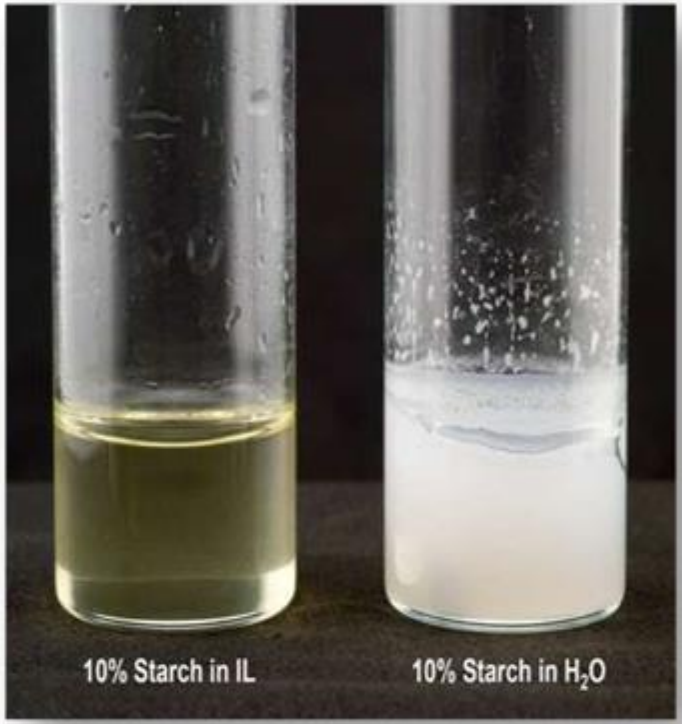
9

EXTRACTION



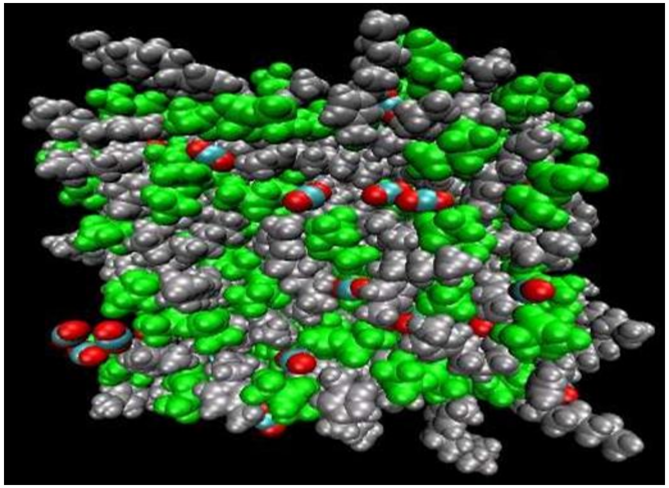
FEW EXAMPLES OF APPLICATIONS

As Solvent



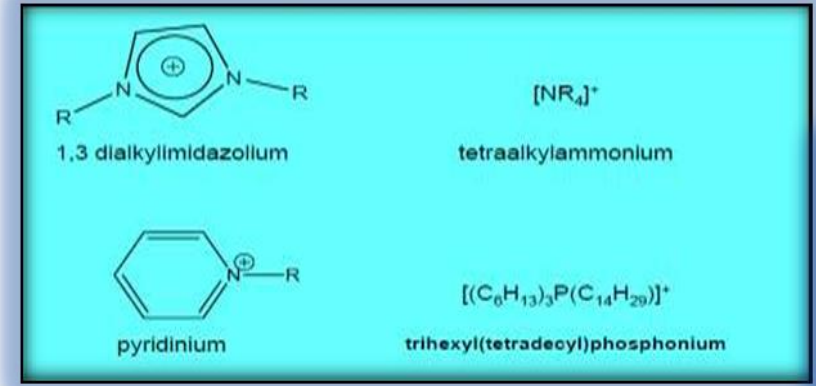
Ionic Liquids as potential solvents

As absorbent

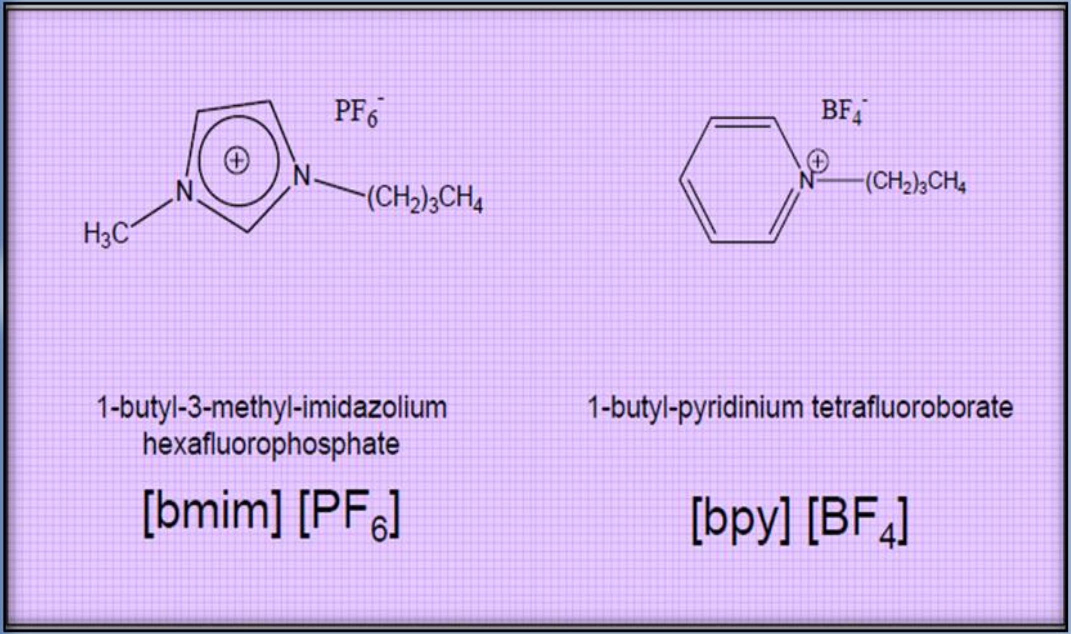


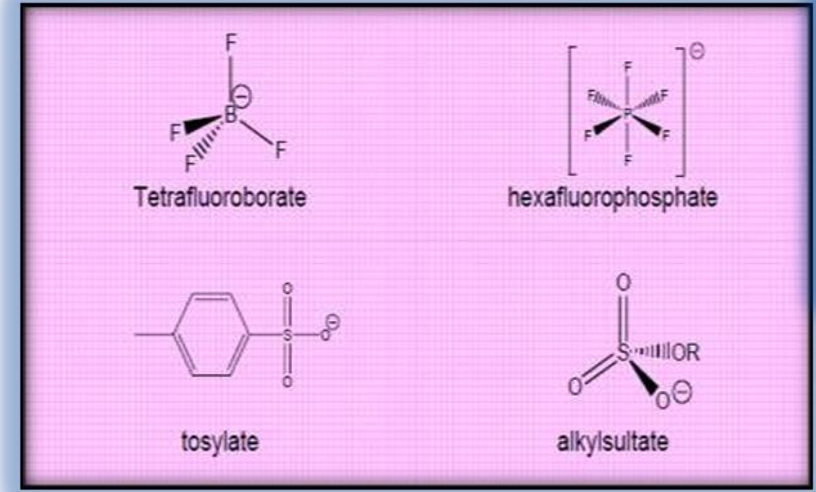
- Model of CO 2absorption by an ionic liquid. The model shows that the anions are controlling absorption in ionic liquids. The green units represent anions and the grey units represent cations.

FEW Magic fluids….examples



structures of cations





structures of anions

HOW TO FORMULATE THIS MAGICAL LIQUID?

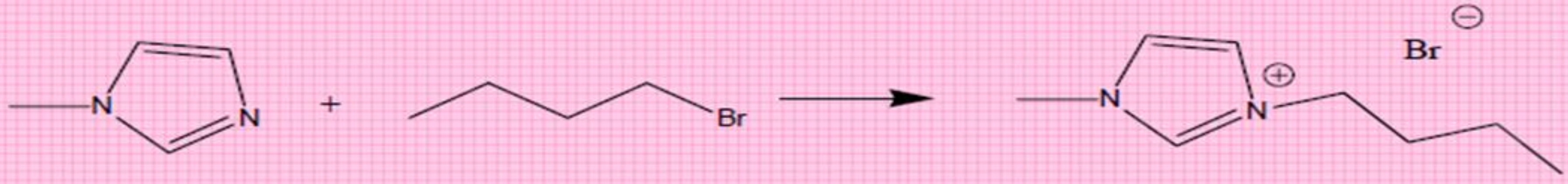
ALKYLATION FOLLOWED BY METATHESIS

ACID-BASE NEUTRALIZATION

ALKYLATION FOLLOWED BY METATHESIS

- ELEVATED TEMPERATURE & REFLUXING SOLVENT APPROACH
- MICROWAVE OR ULTRASONIC SYNTHESIS
- ROOM TEMPERATURE “WAIT & SEE” SOLVENT FREE APPROACH

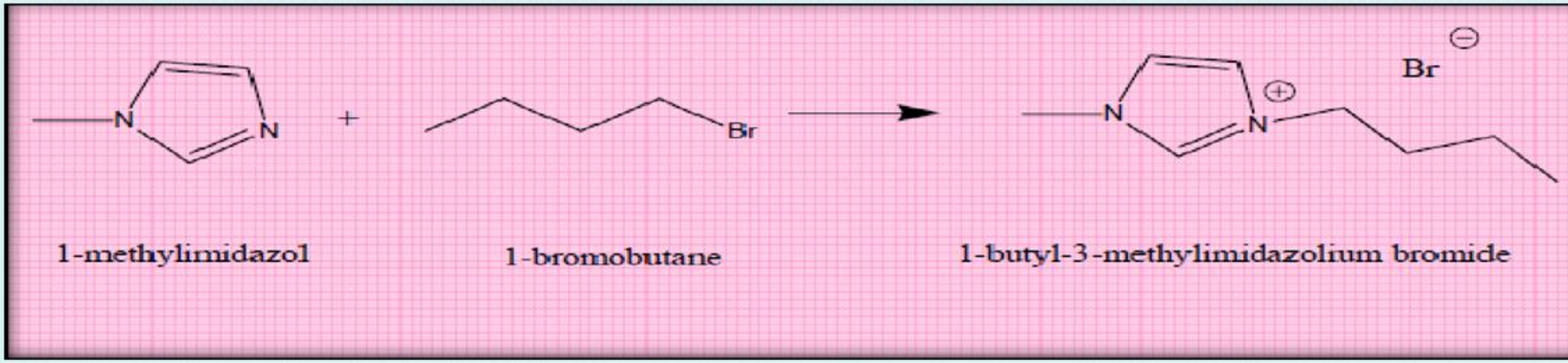
$$NR_3 \xrightarrow{R'X} [NR_3R']^+X^-$$

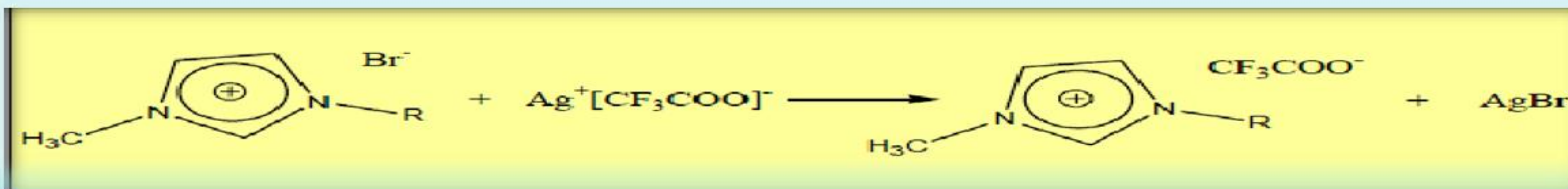


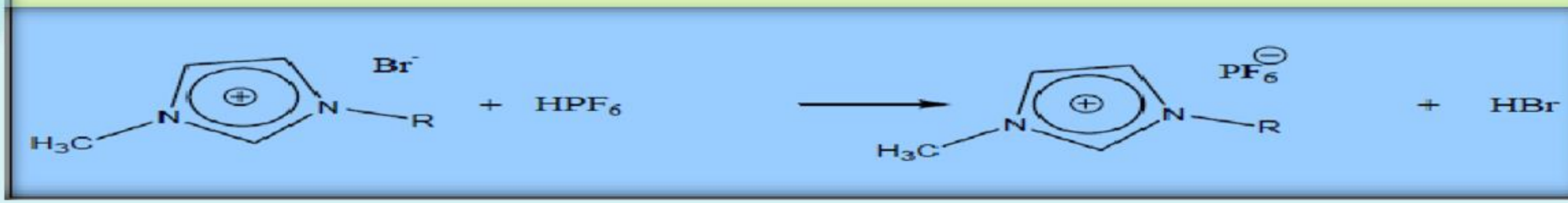
1-methylimidazol 1-bromobutane 1-butyl-3-methylimidazolium bromide

Quaternization reaction

QUATERNIZATION REACTION







ANIONIC EXCHANGE REACTION

Comparison of organic solvents with ionic liquids

Property	Organic Solvents	Ionic Liquid
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tuneable
Chirality	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius–Clapeyron equation	Negligible vapour pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Polarity	Conventional polarity concepts apply	Polarity concept questionable
Tuneability	Limited range of solvents available	Virtually unlimited range means "designer solvents"
Cost	Normally cheap	Typically between 2 and 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity, cP	0.2–100	22–40,000
Density, g/cm^3	0.6–1.7	0.8–3.3
Refractive index	1.3–1.6	1.5–2.2

Advantages of ionic liquids over organic solvents

- ✓ High ionic conductivity
- ✓ Non-flammable
- ✓ Non-volatile
- ✓ High thermal,electrochemical and mechanical stability,
- ✓ Wide temperature range for liquid phase (- 40 to + 200° C)
- ✓ Highly solvating, yet non-coordinating
- ✓ Low toxicity
- ✓ Good solvents for many organic and inorganic materials

Green chemistry

'Utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.'
(Green Chemistry – Theory and Practice, P. T. Anastas & J. C. Warner, Oxford, 1998)

•Ionic liquid-act as solvent in reactions -prevents the waste of solvent.

•Ionic liquid –Reused.

•The miscibility gap of most ionic liquids with alkylated aromatics allows product isolation by simple decantation.

GREEN ASPECTS

The yield for preparing Ionic liquid is as high 99%. (Principle 2)

Seperation of Ionic liquid is easy , just by filtration.

Reaction condition is mild .(Principle 12)

No byproducts in the preparation .(Principle 8)

Ionic Liquids in Organic Synthesis

- Catalytic
- Hydrogenetions
- Hydroformylations
- Heck reactions
- Suzuki coupling
- Stille Coupling

Friedel–Crafts

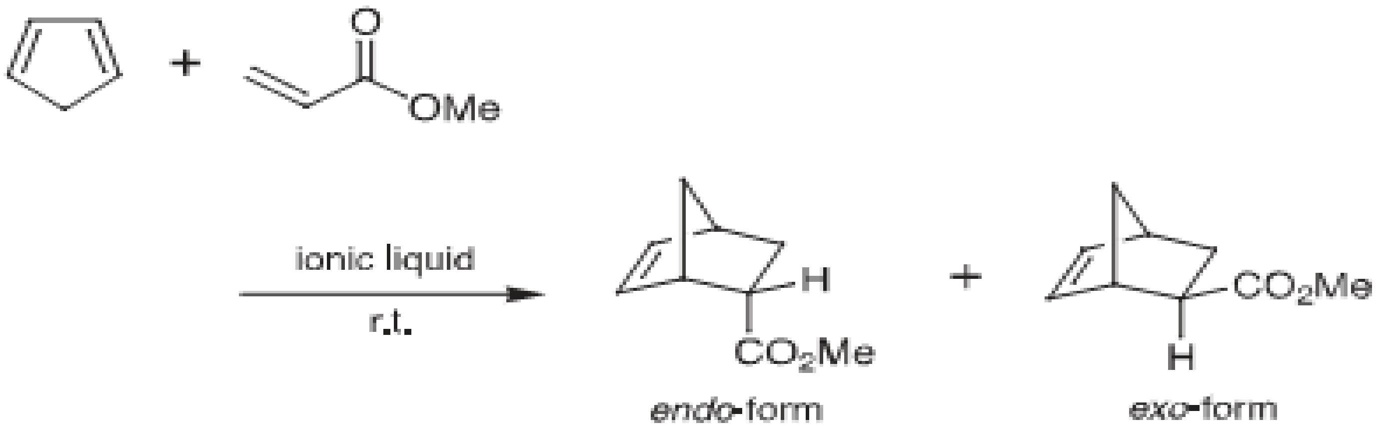
Alkoxycarbonylation

Olefin dimerization

Diels-Alder

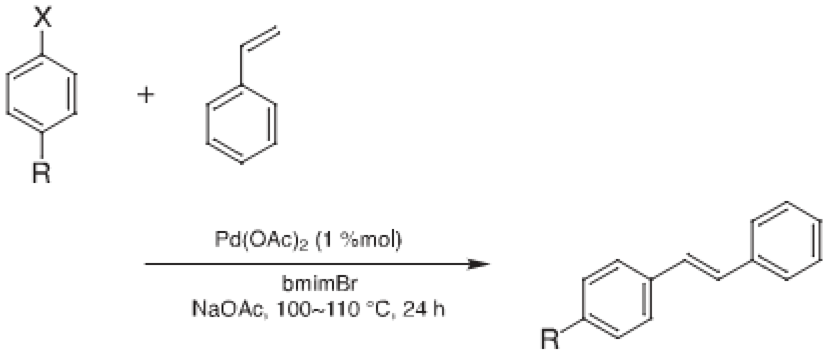
Oxidations

Diels-Alder reaction



ionic liquids	composition (% $AlCl_3$)	time (h)	*endo*/*exo* ratio	Y. (%)	
emimCl/$(AlCl_3)_x$	48 (basic)	22	4.88	32.3	1a)
emimCl/$(AlCl_3)_x$	48 (basic)	72	5.25	95	1a)
emimCl/$(AlCl_3)_x$	51 (acidic)	22	19	53	1a)
emimCl/$(AlCl_3)_x$	51 (acidic)	72	19	79.4	1a)
bmimBF_4	-	72	4.3	91	1b)

Heck Reaction

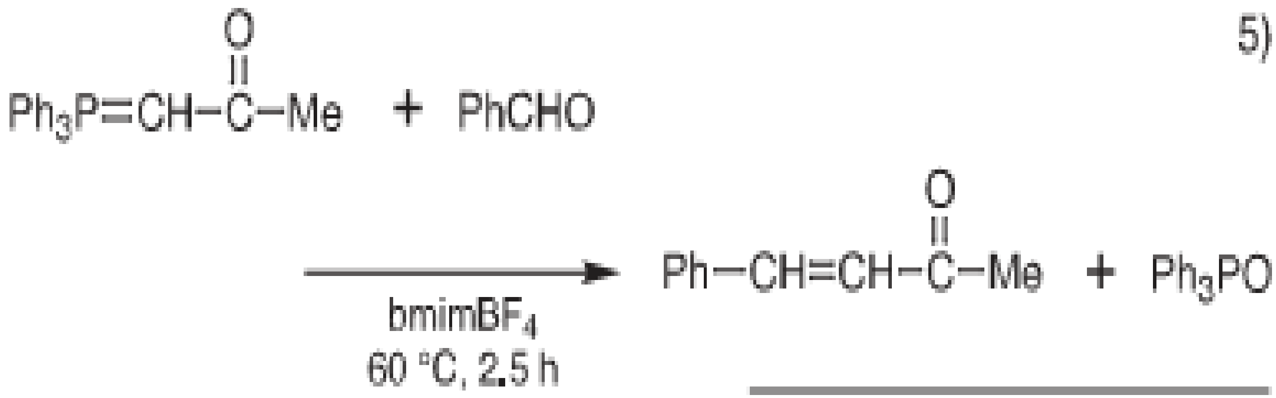


2a)

entry	X	R	conv. (%)	Y. (%)
1	I	H	100	99
2	Br	CHO	100	90
3	Br	MeCO	79	88

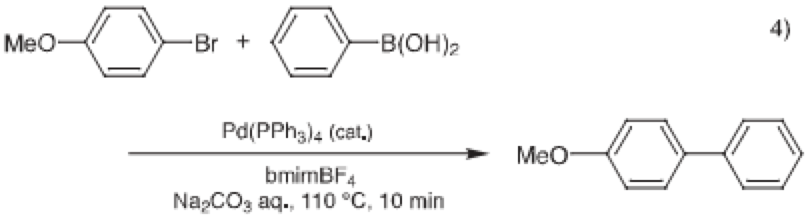
Wittig reaction

5)



	Y. (%)	*E*/*Z*
1st use	82	97/3
2nd use	83	
6th use	91	

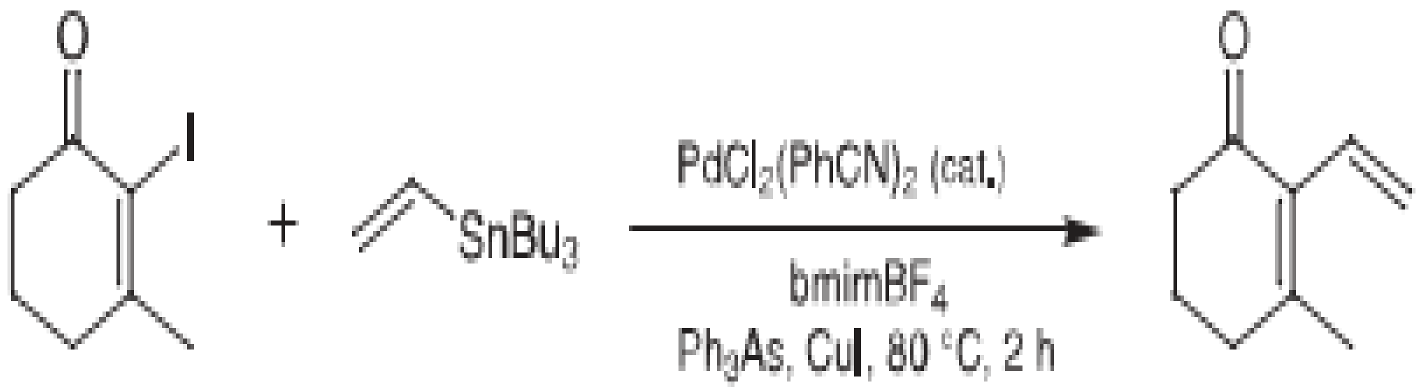
Suzuki-Miyaura coupling reaction



4)

entry	catalytic solution	Y. (%)
1	1st use	81
2	2nd use	89
3	3rd use	77
4	4th use	82

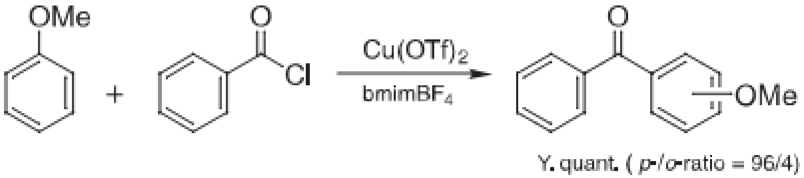
Stille reaction



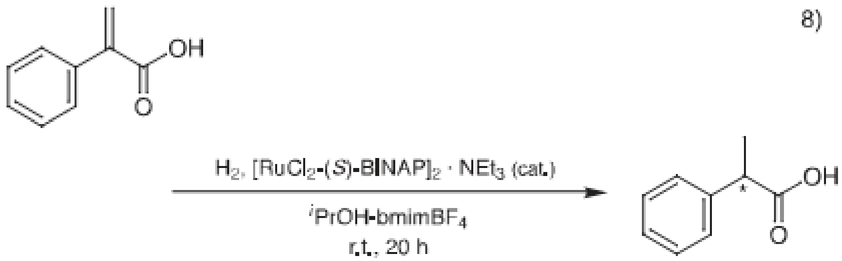
6)

	Y. (%)
1st use	82
2nd use	78
3rd use	72*

Friedel-Crafts reaction

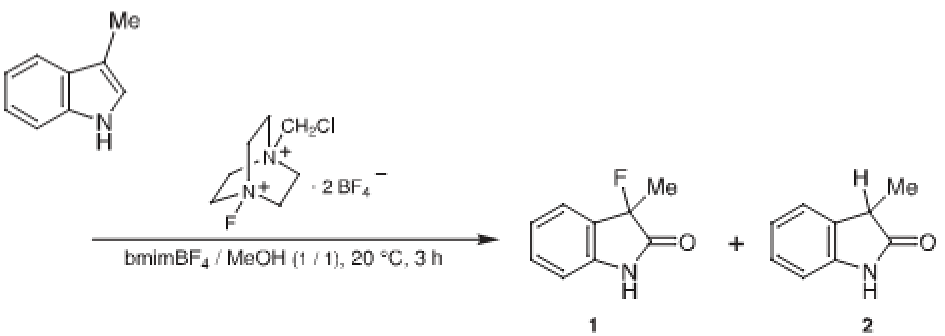


Hydrogenation



	P (atm)	conv. (%)	% *e.e*
1st use	50	100	78 (*S*)
2nd use	75	100	84 (*S*)
3rd use	25	90	79 (*S*)
4th use	100	95	67 (*S*)

Fluorination



entry	solvent	cosolvent (1/1)	temp. (°C)	time (h)	1 (%)	2 (%)	
1	MeCN	H_2O	r.t.	overnight	71	small amount	10a)
2	$bmimBF_4$	MeOH	20	3	99	-	10b)

Green Aspects

- The yeild for preparing Ionic liquid is as high 99%. (Principle 2)
- Seperation of Ionic liquid is easy , just by filtration.
- Reaction condition is mild .(Principle 12)
- No byproducts in the preparation .(Principle 8)

Application

- •Ionic liquids –used in microreactors to synthesize & purify extremely reactive organometallic compounds (using the Green Chemistry principles.)

- •Ionic liquids -used for efficient heat storage and transfer in solar thermal energy systems.

- •Ionic Liquids -dispersing agents in paints to enhance
- appearance and drying properties

- •1-butyl-3-methylimidazolium hexafluorophosphate-used-non aqueous electrolyte medium -recovery of uranium in spent fuel rods.

- •Some ionic liquids -advantage of both homogeneous and heterogeneous catalysts.

Conclusion

- Ionic liquids ,as the new materials of multifunction , are widely used in various of fields.

- Environmently-friendly reaction process have vigorously been studied from the standpoint of green chemistry and based on the properities of easy separation , low toxicity , selective miscibility , ILS play an important role in organic synthesis as the green alternative solvent.