Ionic liquids
Part I: general properties

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Outline of the presentation

- Presenting my group
- Ionic Liquids
  - Definition, structure, basic properties
  - Some practical hints
  - Focus on solvation of ions in ILs
  - Two examples of « applications »

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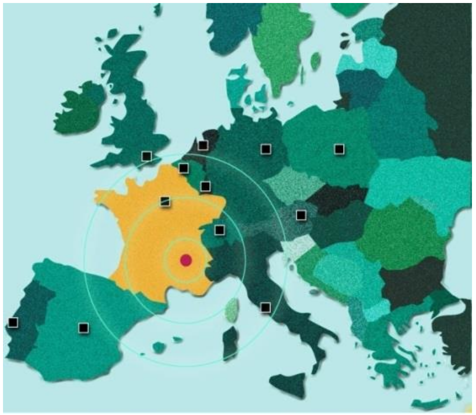
Where and what ?



LEPMI:
Laboratory of Electrochemistry, Physico-chemistry, Materials, Interfaces

Grenoble is a great research place: ESRF, CEA, ILL, Minatec …

Sub-group at LEPMI:

- Recycling of metals by hydro/solvo metallurgical means
- Electrochemistry
- Life cycle analysis
- Fundamental physico-chemistry of metals in ionic liquids

Who ?

Nadine Commenges-Bernole

Jean-Pierre Magnin

Lenka Svecova

Eric Chainet

Fundings

- French ministry of research.
  - Ph-D funding, Ln electrodeposition; end oct. 2017

- Labex CEMAM: french 'center of excellence' for multifunctional architectured materials
  - Ph-D funding, NiMH batteries study; end oct. 2018

- European funding, driven by ADEME in France: french agency for environment and energy management; 36 months;
  collaboration with Portugal (Pr. J. Coutinho).
  - Post-doc funding 18 mo, IL-ABS and NiMH batteries

Position now open

- Past fundings (post-doc. fellows, 2 years):
  - Strasbourg University (end: april 2016)
  - Marie Curie fellowship from Europe (end: feb. 2016)

EXchange on Ionic Liquids: EXIL

- COST Action : Cooperation in Science and Technology

- Direction: **Prof. Rasmus Fehrmann**

- French committee
  - Catherine Santini (Vice-President)
  - Margarida Costa Gomes
  - Philippe Hapiot
  - Isabelle Billard

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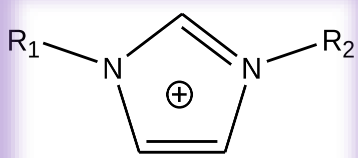
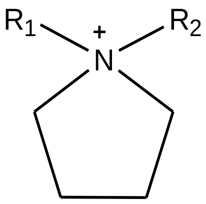
ILs: definition, chemical structure

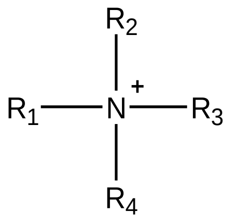
ILs are salts with melting T below 100°C



1,3-dialkyl-imidazolium



dialkylpyrrolidinium



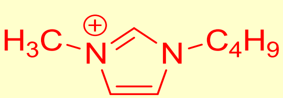
ammonium quaternaire

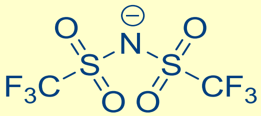
BF_4^-, PF_6^-, Cl^-, Br^-, NO_3^-

$CF_3SO_3^-$, $(CF_3SO_2)_2N^-$

$[CF_3SO_2NCH_3SO_2]^-$

Cat⁺ Ani⁻:





$C_1C_4im^+$ Tf_2N^-

Comparison:
NaCl T_m= 800 °C;
LiCl-KCl T_m= 350 °C

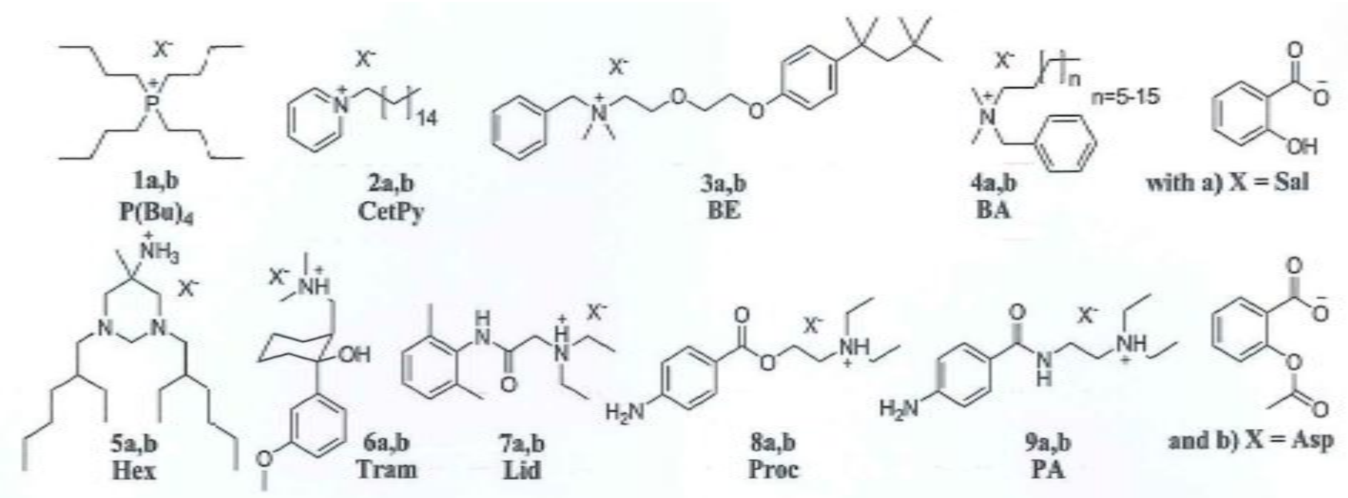
An incredible variety of cations since long ago, although choice is limited for dedicated applications. Recently, anion variety increased.

A long way towards nowadays ILs

- $CH_3CH_2NH_3^+NO_3^-$ T_m= 12°C 1914
- Batteries for US Air Force, 'low T' electrolytes since 1960
- NaCl-$AlCl_3$ T_m=107°C
- ButylpiridiniumCl-$AlCl_3$ T_m= 40°C (1:1) 1978
- C_1C_2imCl-$AlCl_3$ T_m < 0°C 1984
- C_1C_2imBF_4 T_m = 6°C 1992

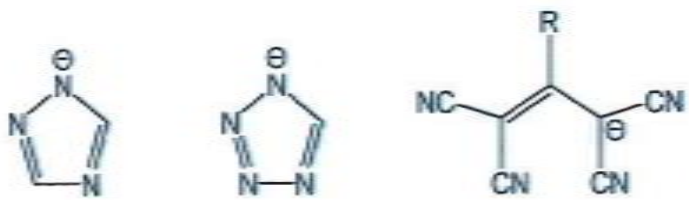
As long as chloroaluminates are present,
compounds are not stable towards air and water

Some examples of structural diversity

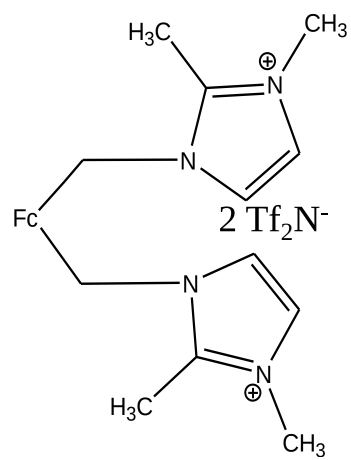


Cations:
1,2,3,4, 5 : antibacterial
6: painkiller
7,8: local anaesthetic
9: antiarythmique
Anions:
a) salicylate
b) acetylsalicylate

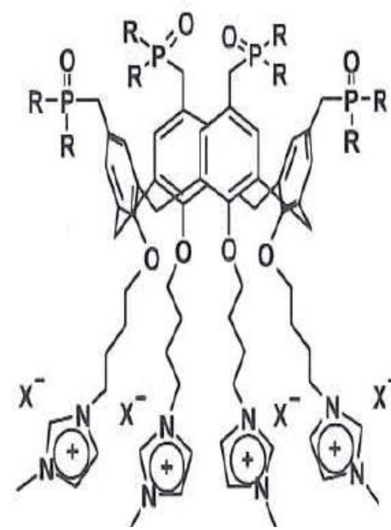
Only 5a and 6a are not ILs.



Yoshida et al., PCCP, 12(2010)1675



With ferrocene

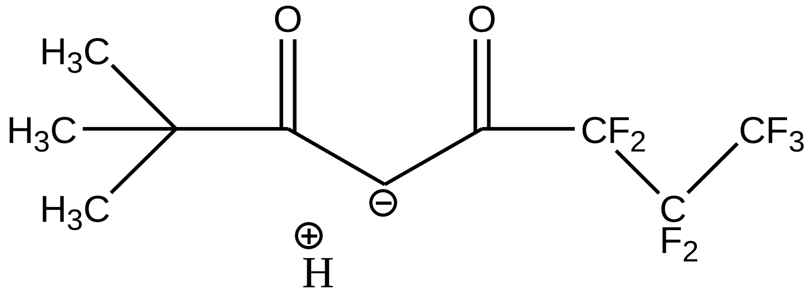


LI+calixarene

Bica et al., PCCP, 12(2010)2011; Miroshnichenko et al., P, S and Si, 186(2011)903.

A few (less classical) anions

- I^-, I_3^-, I_5^-, I_7^-, I_9^-
- $(C_2F_5SO_2)_2N^-$
- $CF_3BF_3^-$, $C_2F_5BF_3^-$
- $(CF_3SO_2)N(COCF_3)^-$
- AsF_6^-, SbF_6^-, WF_7^-, $Eu(Tf_2N)_4^-$
- $N(CN)_2^-$
- Perfluoroalkyl β-diketones



General physico-chemical properties

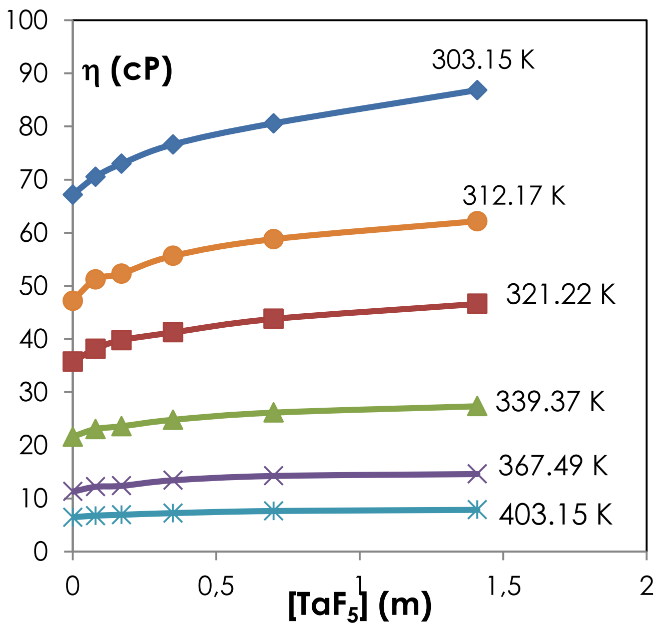
Owing to IL versatility, all their general properties can vary along a yes/no dilemna. The only two exceptions are : ILs are salts, therefore *viscous* *conducting* materials.

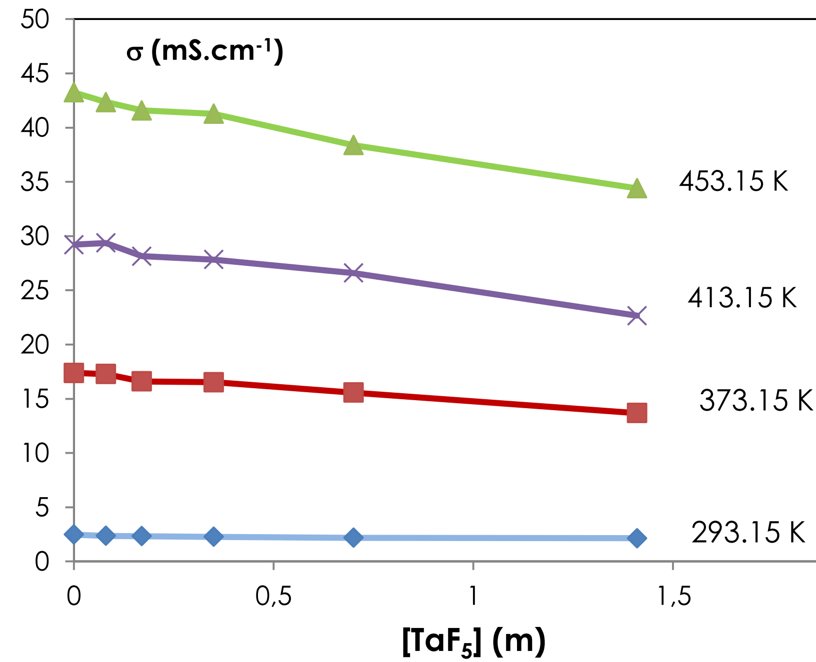
- Pro
  - Large electrochemical window
  - Large liquidus
  - High conductivity
  - Miscibility to other solvents
- Cons (?!)
  - High viscosity
  - Cost
  - Too numerous ILs
- And unknowns
  - Toxicity, flammability
  - biodegradability, edibility …

Melting points -liquidus

- Experimental difficulties
  - Surfusion is not rare and can spread over 200°C
  - Most ILs do not cristallise
  - Isomorphism
- Examples
  - C_2C_1imTf2N T_m = -50°C; -21°C; -16°C; -15°C
  - C_4C_1imTf_2N T_m = -6°C; -3°C
  - C_5C1imTf_2N T_m = -9°C
  - C_6C1imTf_2N T_m = -6 °C
  - C_7mimTf_2N T_m = 7°C
  - C_9mimTf_2N T_m = 14°C
- Liquidus
  - ILs decompose before boilling
  - Some are volatile or distillable

Viscosity and conductivity





Do not expect to pipette ILs easily, do it by weight

Nahra et al. Fluid Phase Equilibria, 415(2016)101

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Providers and prices

- Big companies
  - Sigma-Aldrich, Merck et al.

Purity is questionable

but may be sufficient

- Small firms
  - Solvionic, Iolitech,

Spectroscopic purity; ILs by order

- ILs are costly !
  - $C_1C_4im^+Tf_2N^-$: 1kg (≈ 700 ml) for 1.5 k€

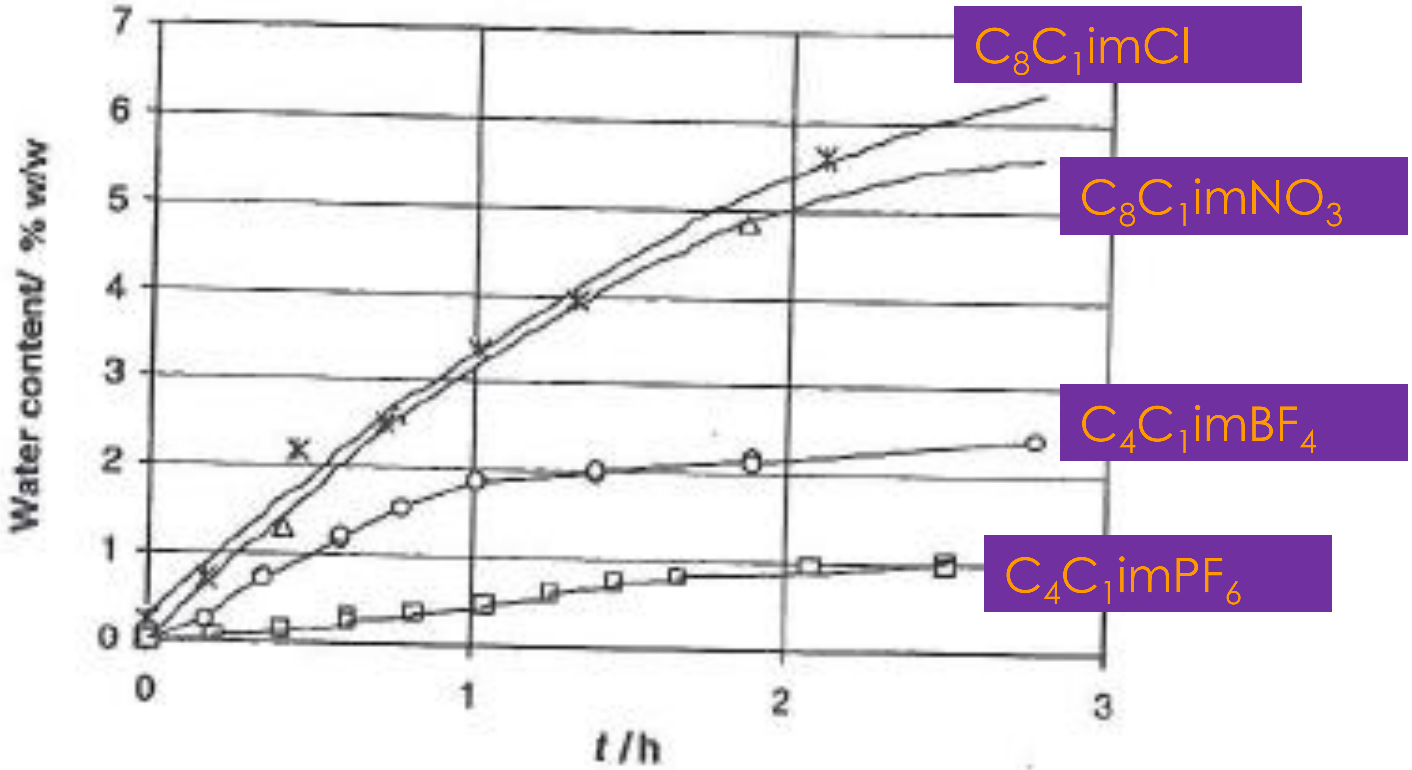
Practical tips

Main impurities are water and halides but other compounds from reactants can be deleterious. They have a tremendous impact on ILs' properties, especially for spectroscopic studies.

purified "home maid" purchased (2002)

ILs are hygroscopic

ILs absorb (+ or - slowly) atmospheric water

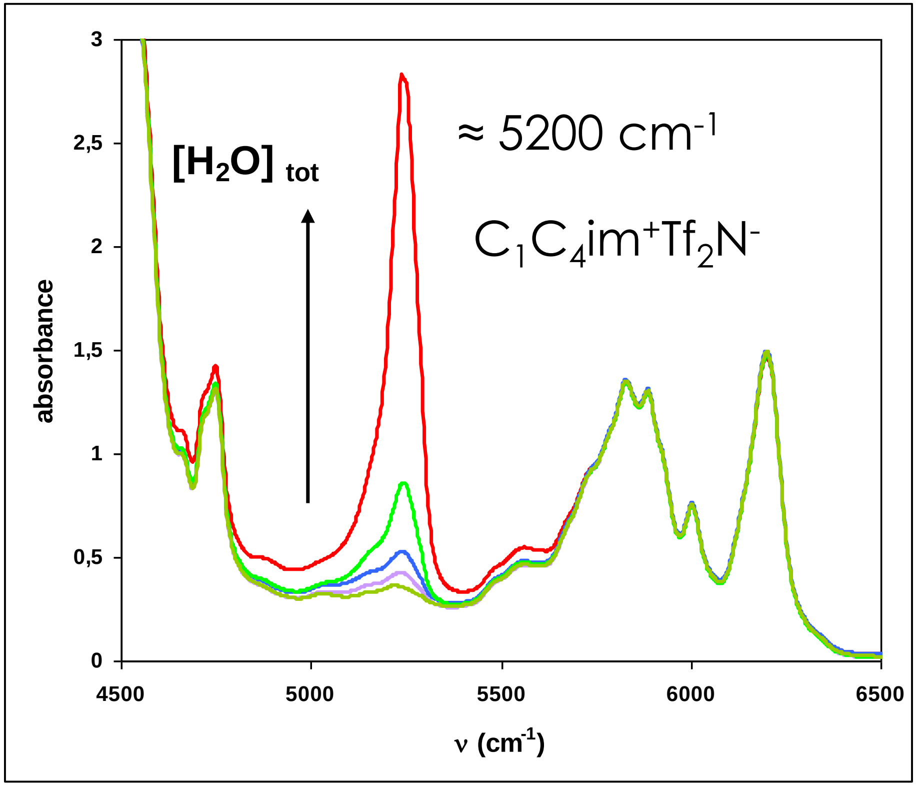


$C_1C_4imTf_2N$: 12000 ppm of H_2O at saturation

Vacuum lines are useful

Determining water amount in ILs

- Karl-Fischer limit: ≈10 ppm
- IR limit: ≈ 50 ppm



This gives access to the total water amount, either free or bound to ions.

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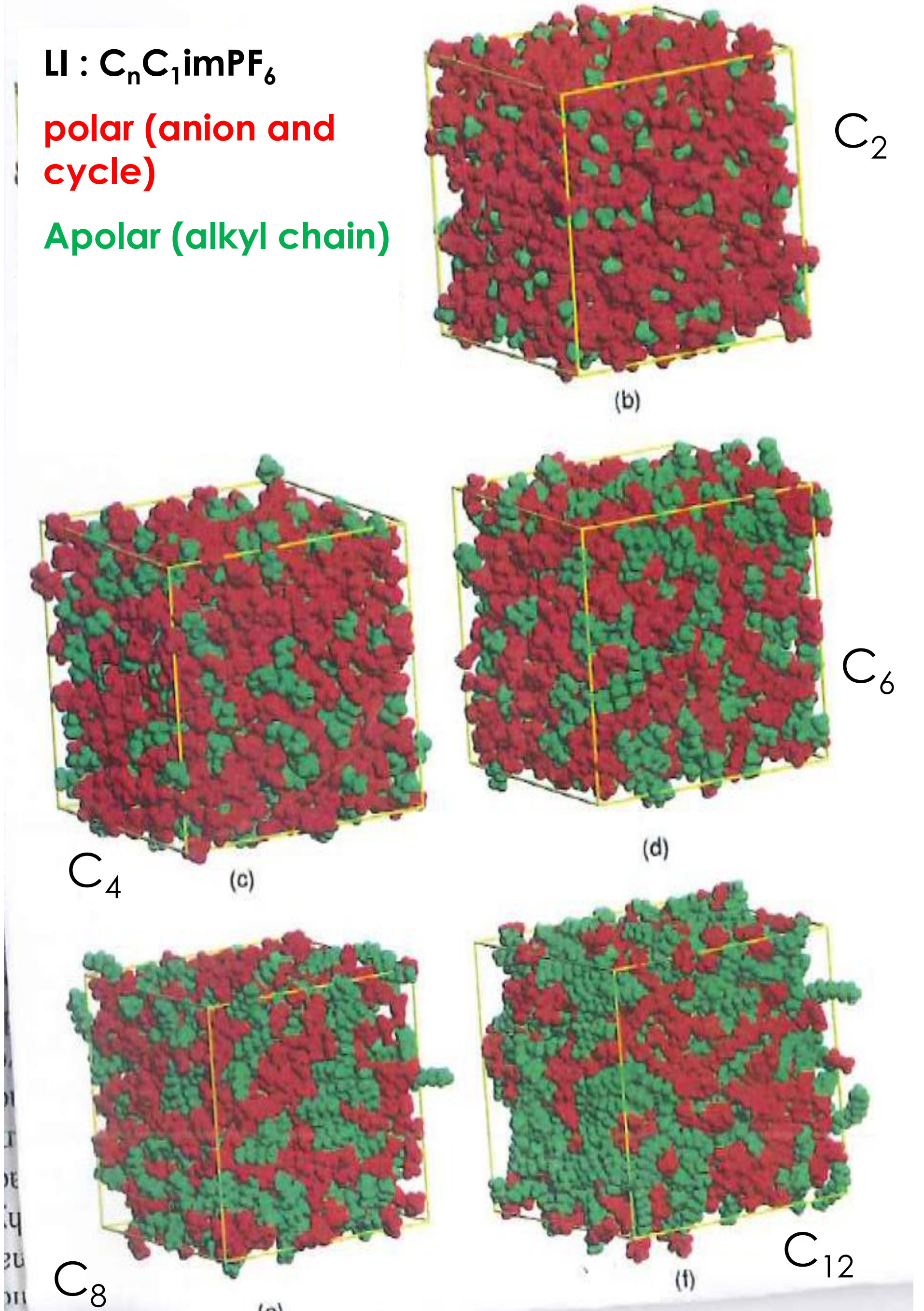
ILs are nanostructured compounds

Microscopic heterogeneities lead to dual solvation properties: ILs based on $C_nC_1im^+$ solvate ions *and* neutral species



Canongia et al., J. Phys. Chem. B, 110(2006)3330

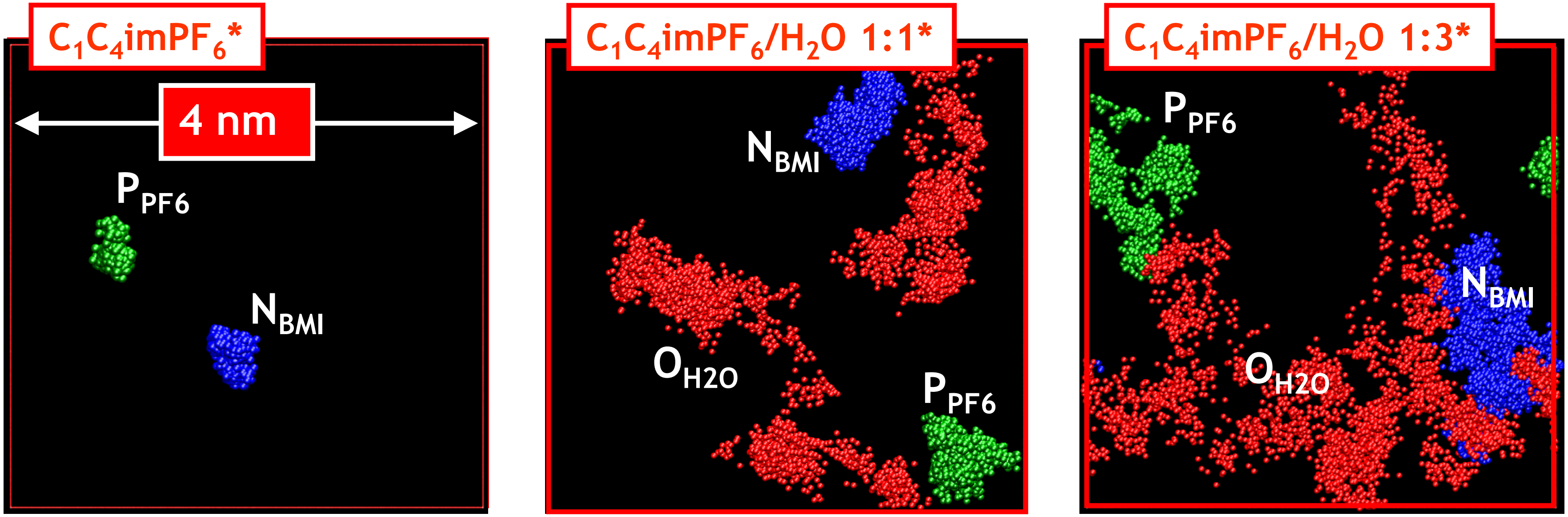
Chaumont et al., J. Mol. Liquids, 131/132(2007)36

Jiang et al., J. Phys. Chem. B, 111(2007)4812

Chaumont et al., J. Mol. Liquids, 131/132(2007)36

Chaumont et al., Inorg. Chem. 43(2004)5891

Dynamics and humidity for $C_1C_4imPF_6$ at 300 K

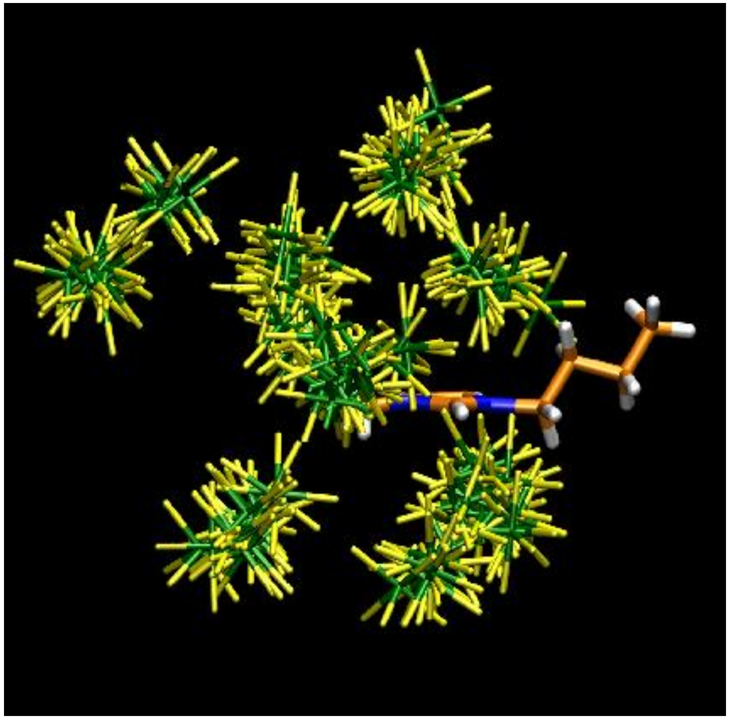


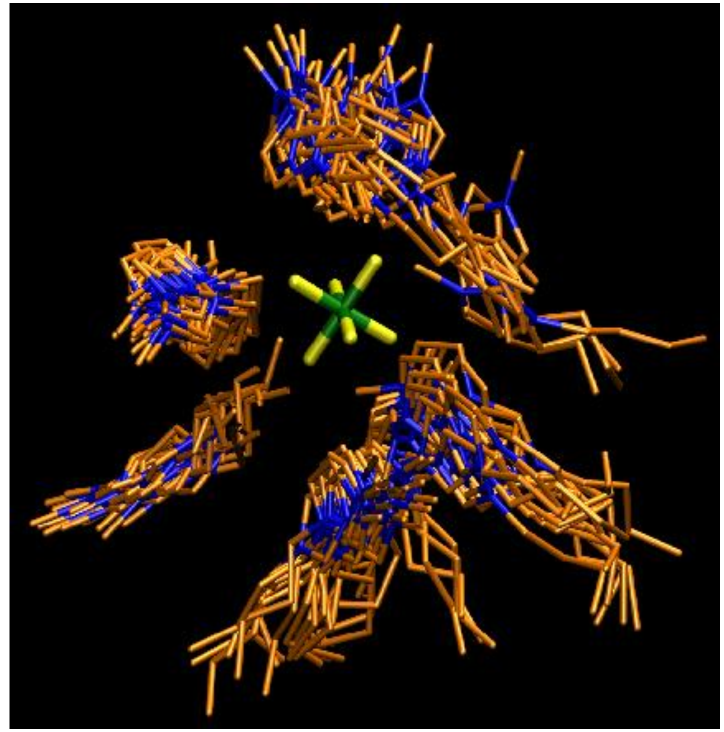
Coefficients de diffusion (10^{-7} cm^2 s^{-1})

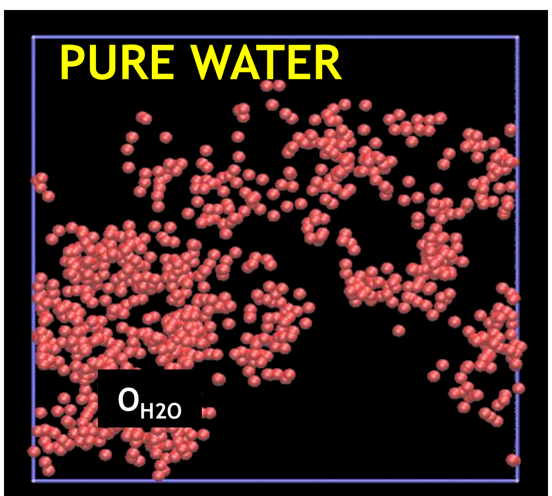
☞ H_2O increases diffusion

*Views cumulated over 2 ns

Ils are 'almost frozen' liquids



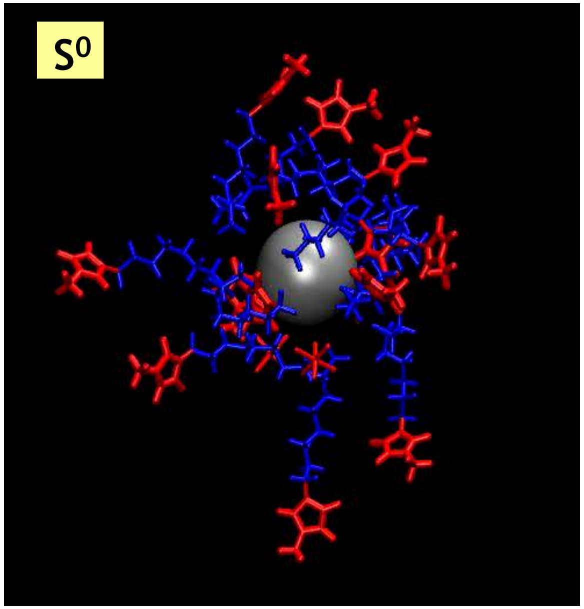


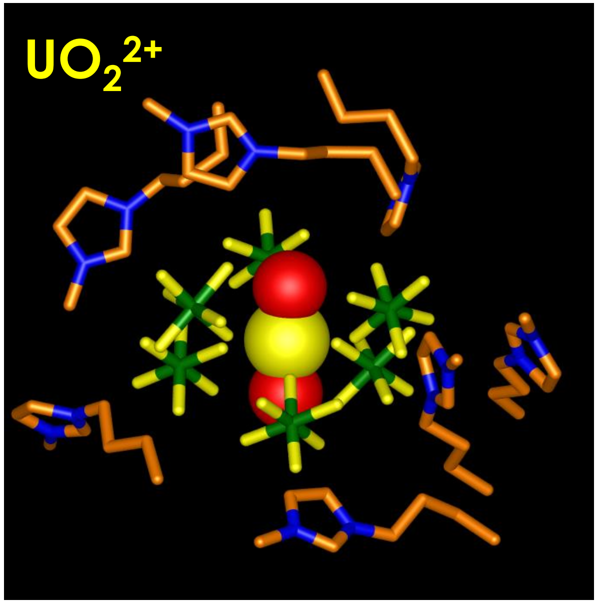


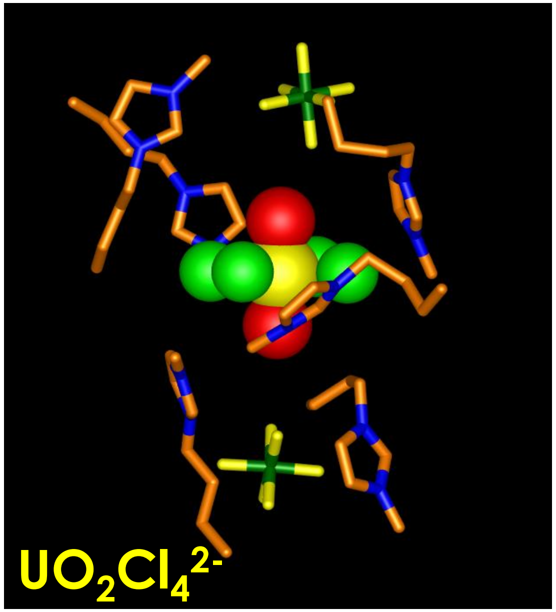
Dynamics of $C_1C_4imPF_6$ (1ns / 300 K)

This is the 'ionic' (molecular) scale transcription of experimental results on viscosity and diffusion coefficients

Solvation depends on charge







Dual solvation :

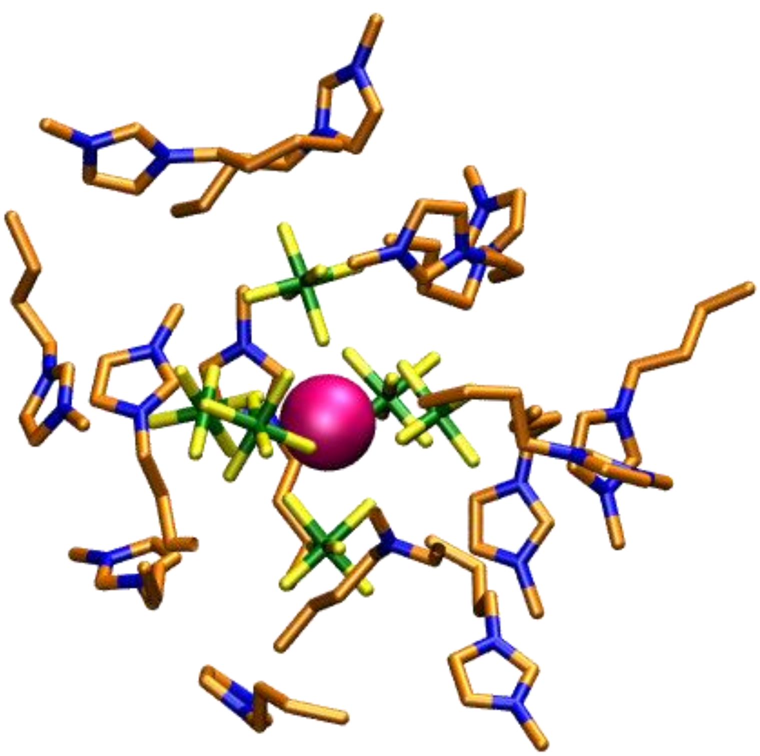
alkyle chains solvate 'hydrophobic species' S^0

charged parts solvate 'hydrophilic species'

solvation as an onion structure

Open questions for (metallic) cations

- Is coordination number maintained ? **YES**
- What are the real charges ?
- Which are the diffusive species ?



Eu^{3+}

$[Eu(PF_6)_6]^{3-}$

$[Eu(PF_6)_6(C_1C_4im)_{13}]^{10+}$

Eu^{3+} in $C_4C_1imPF_6$

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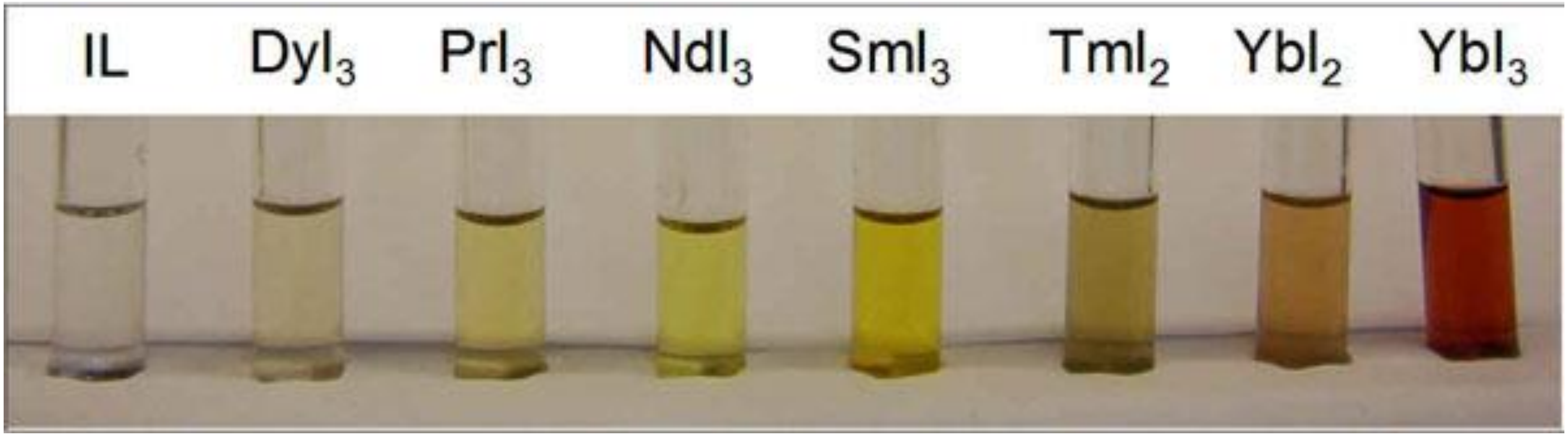
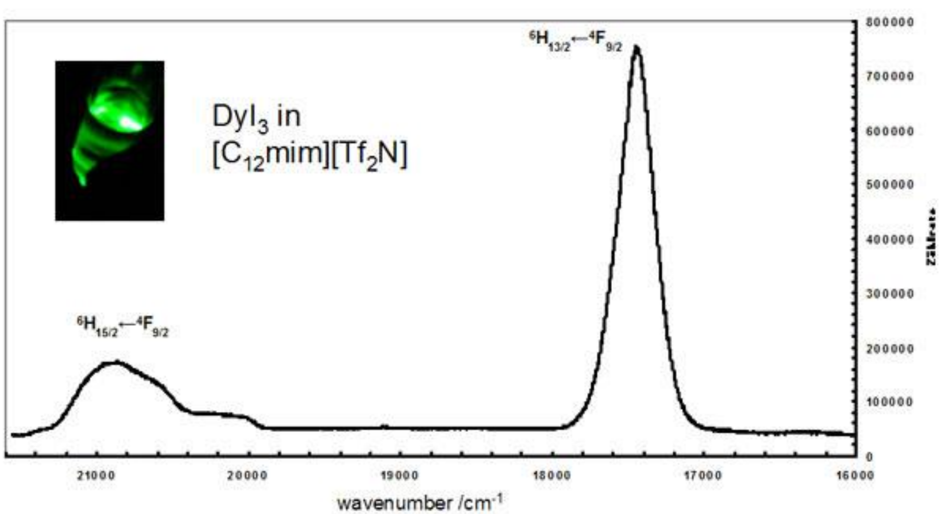
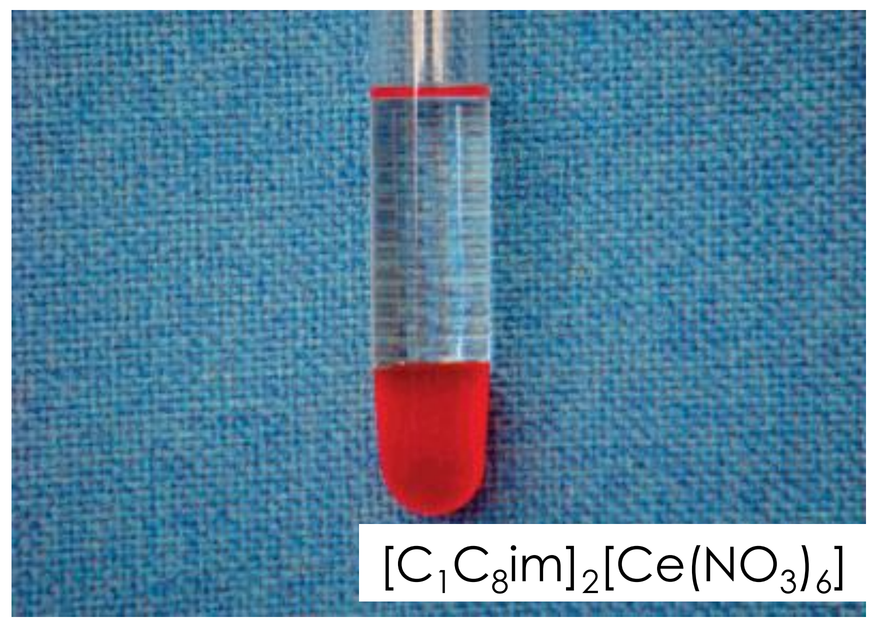
Lanthanides in ILs

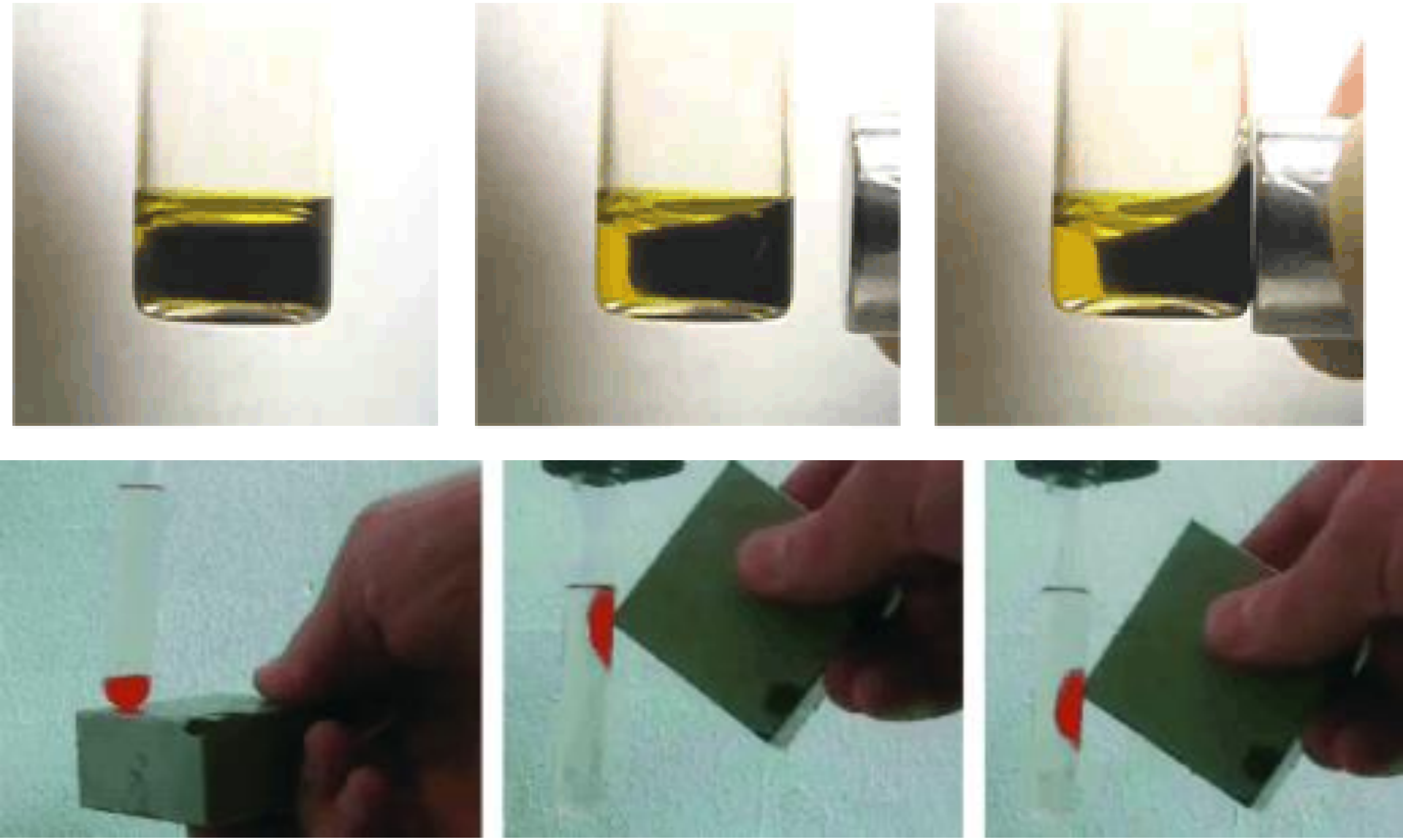






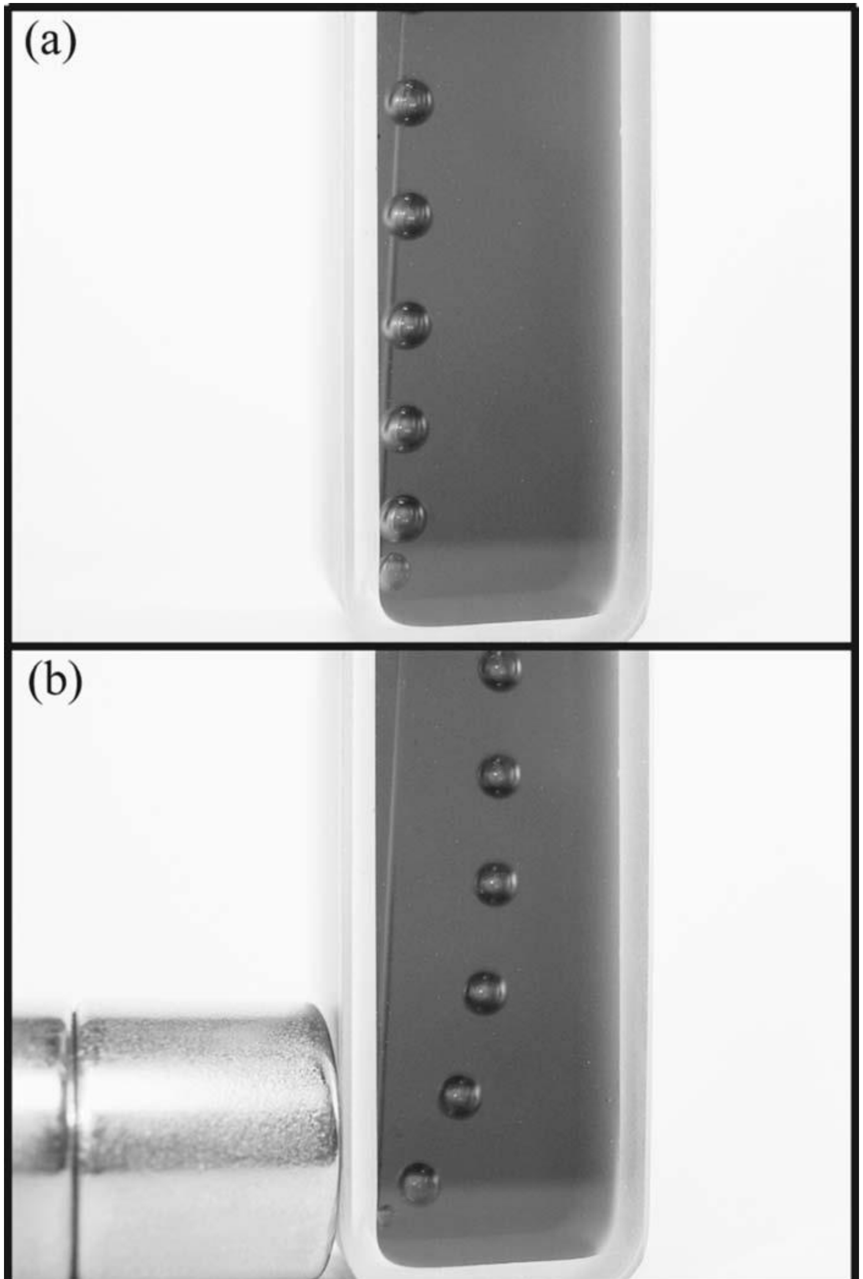
WEB site, Prof. A. Mudring.

Change of rheological properties under magnetic field



Mallick et al., Angew. Chem. Int. Ed., 47(2008)7635; LI avec Dy; see also: Del Sesto et al., Chem. Comm. (2008)447

Example of ILs as funny materials



N_2 bubbles in a magnetic IL $C_1C_4imFeCl_4$are déviées:

It depends on viscosity, B gradient, bubble size and density …

Potential application : dynamical separation of materials as a function of their density

Okuno et al., Appl. Phys. Lett., 89(2006)132506

Back-home message

- Tremendous variety
  - You can graft (almost) whatever you could dream of on the IL skeleton
  - Thus, get whatever you can imagine as physico-chemical properties
- A supramolecular nanostructured environment
  - Ideal for chiral synthesis, nanoparticles size control, unexpected reactions etc…

HOWEVER
ILs are not 'ajustable' and
their properties are not 'tunable'
as we do not understand relationships
between structures and properties.
This is merely trials and failures

Thank you for your attention.