POLITECNICO DI MILANO 150°

Conference COST Action CM1206 EXIL

POLITECNICO DI MILANO





Ionic Liquids at Polimi: basic research and applications

Andrea Mele

Department of Chemistry, Materials and Chemical Engineering "Giulio Natta"
Politecnico di Milano - ITALY

Politecnico di Milano was established in 1863 and is the largest technical university in Italy.

Politecnico di Milano is divided into

3 Schools of Architecture

6 Schools of Engineering

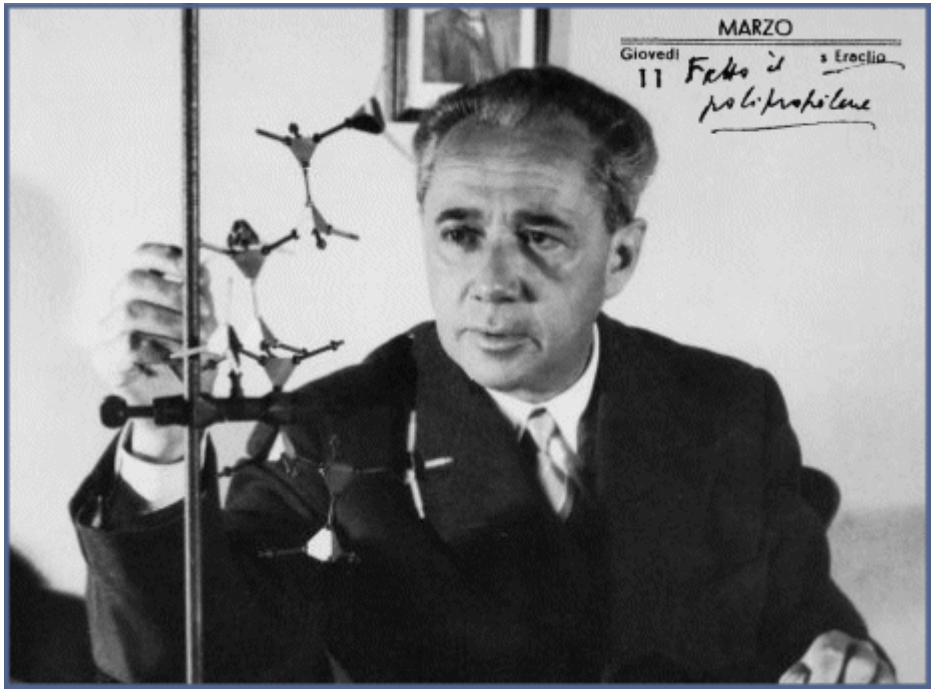
Teaching levels and degrees:

Bachelor (Laurea - 3 years, 1st level)

Master (Laurea magistrale, 2 years after Laurea, 2nd level)

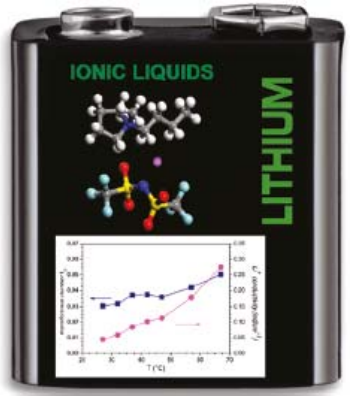
PhD (Dottorato di Ricerca)

The Department of Chemistry, Materials and Chemical Engineering was established in 2001 through unification of three pre-existing chemistry-oriented departments.



One of these was the scientific home of the Chemistry Nobel Prize winner Giulio Natta (shared with K. Ziegler in 1963, for stereospecific polymerization).

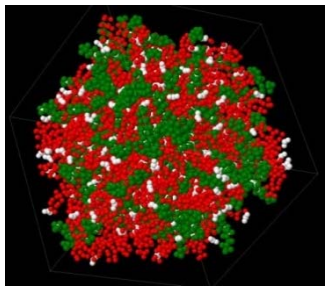
ILs@polimi: Research lines



New systems for LIB

NMR – MD – Electrochemical methods

WG3



Local structure and dynamics

NMR – MD - WAXS – SAXS

WG2

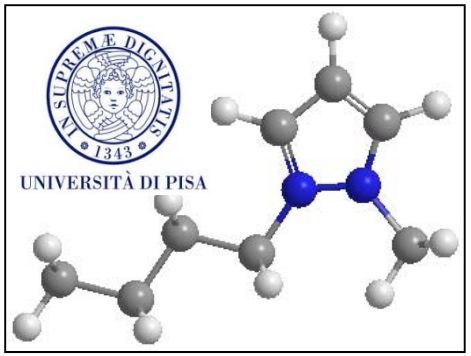
Biocatalysis in ILs

Phospholipids synthesis

Lignocellulosic materials processing

Synthesis and characterization of new ILs

WG1



Basic research: Local structure by NOE data and MD simulations

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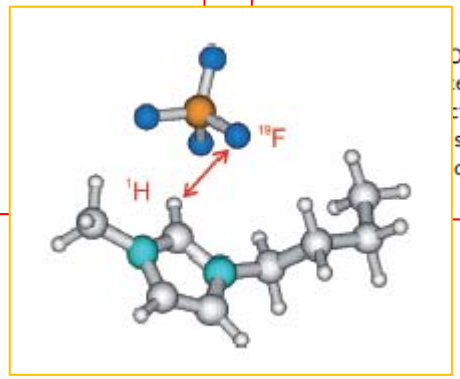
Communications

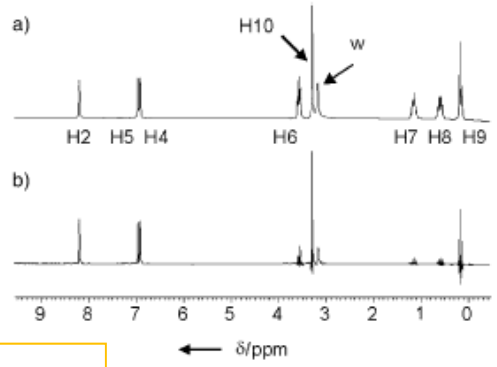
Structure of Ionic Liquids

The Structure of a Room-Temperature Ionic Liquid with and without Trace Amounts of Water: The Role of C–H···O and C–H···F Interactions in 1-*n*-Butyl-3-Methylimidazolium Tetrafluoroborate**

Andrea Mele, Chieu D. Tran, and Silvia H. De Paoli Lacerda*

Angew. Chem. Int. Ed. **2003**, *42*, 4364–4366





OE difference experiment carried out on compound
e spectrum ("off resonance"). Trace b) $^{1}H\{^{19}F\}$
trum (vertical scale magnified 32 times with
signals of H2, H4, H5, and water (w) are in pure
of heteronuclear NOE. The other signals are sub-

Interaction of Water with the Model Ionic Liquid [bmim][BF_4]: Molecular Dynamics Simulations and Comparison with NMR Data

Margherita Moreno, Franca Castiglione, Andrea Mele,* Carlo Pasqui, and Guido Raos*

Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, 20131 Milano, Italy

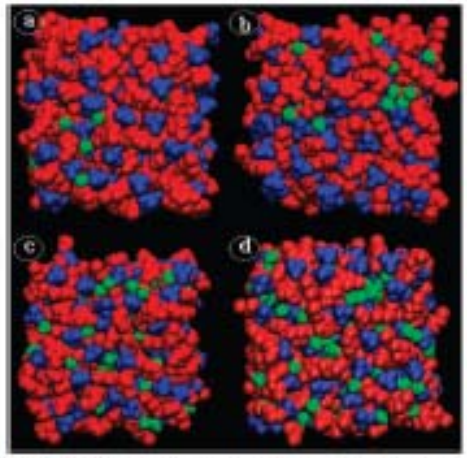
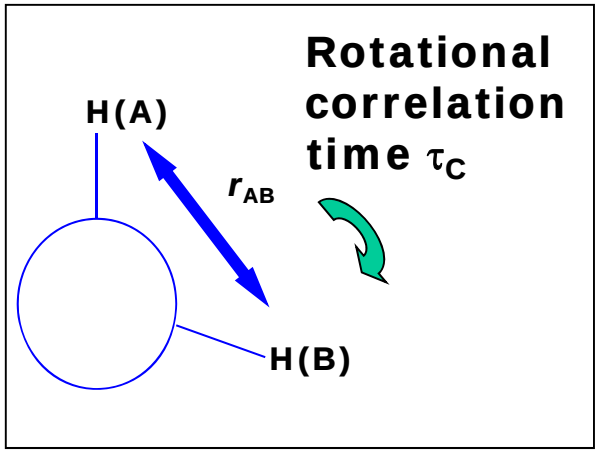


Figure 3. Representative snapshots from the MD simulations of [bmim][BF_4]/water systems using FF1: (a) 1:8 mixture, (b) 1:4 mixture, (c) 1:2 mixture, (d) 1:1 mixture. Color code: water in green, cations in red, anions in blue. Hydrogens are not shown, for clarity. The figures have been generated with VMD.[33]

Basic research: Local structure by NOE data and MD simulations



Intramolecular spin-spin dipolar relaxation

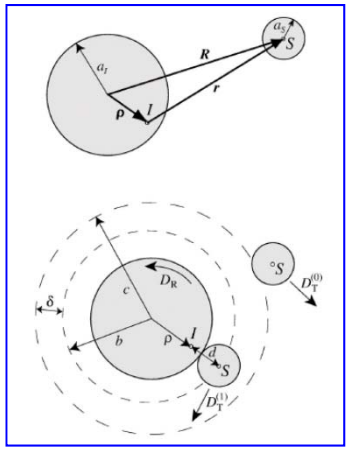
Model: Intramolecular cross-relaxation (NOE) dominated by molecular tumbling.

Distance dependence: r^{-6}

Consequence: non vanishing NOEs for r < 4Å

Only short-range interactions. High selectivity.

Neuhaus & Williamson *The NOE in structural and conformational analysis*. Wiley



Intermolecular spin-spin dipolar relaxation

Model: interacting molecules as hard spheres undergoing rotational and translational diffusion. B. Halle *J. Chem. Phys.* **2003**, *119*, 12372

Intermolecular cross-relaxation (NOE) dominated by translational diffusion

Distance dependence: r^{-1}

Consequence: also long-range interactions may give rise to observable intermolecular NOEs. Low selectivity.

VIP Ionic Liquids

DOI: 10.1002/anie.201302712

From Short-Range to Long-Range Intermolecular NOEs in Ionic Liquids: Frequency Does Matter**

*Sonja Gabl, Othmar Steinhauser, and Hermann Weingärtner**

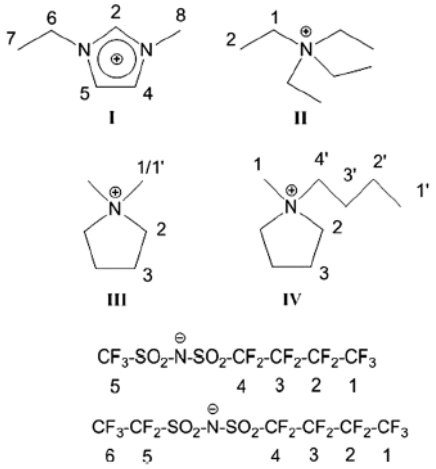
Basic research: Local structure and dynamics

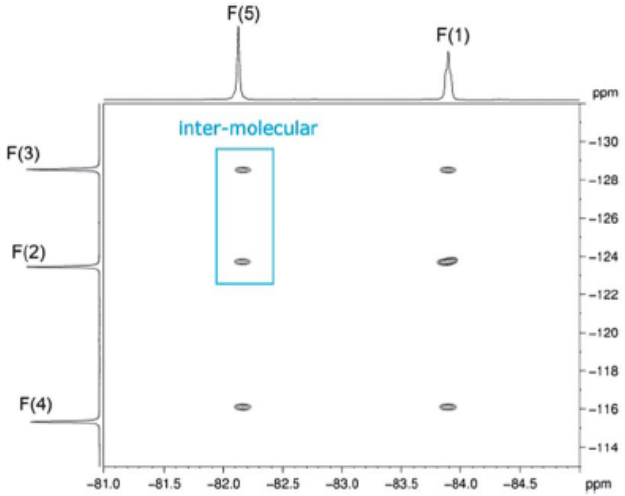
Faraday Discussions
Cite this: DOI: 10.1039/c3fd00056g
RSC Publishing
167/20

PAPER

Mesoscopic structural organization in triphilic room temperature ionic liquids

Olga Russina,[a] Fabrizio Lo Celso,[b] Marco Di Michiel,[c] Stefano Passerini,[d] Giovanni Battista Appetecchi,[e] Franca Castiglione,[f] Andrea Mele,*[f] Ruggero Caminiti[a] and Alessandro Triolo*[g]





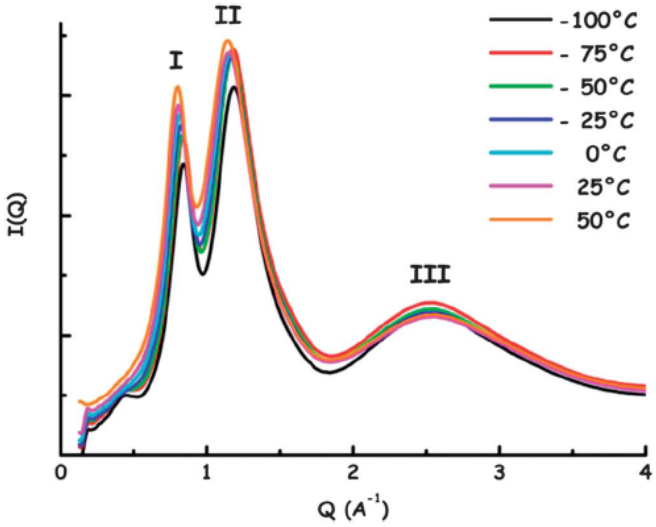


Fig. 3 SWAXS data from tetraethylammonium [IM_{14}] (**II**), at different temperatures (173–323 K).

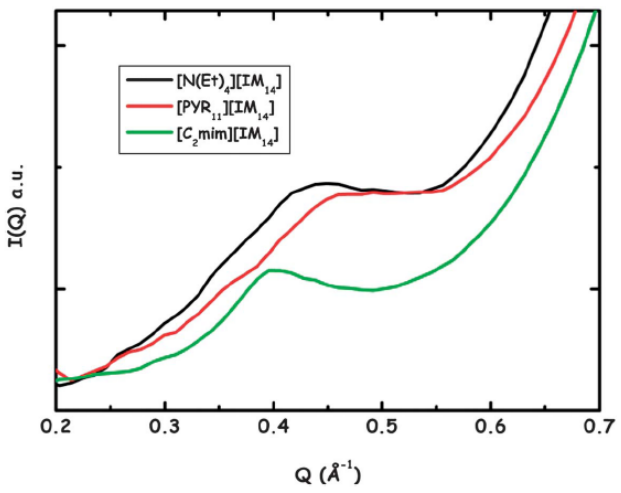


Fig. 5 Low *Q* portion of the SWAXS patterns from samples **I–III** at −100 °C.

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

dx.doi.org/10.1021/jz400617v | J. Phys. Chem. Lett. 2013, 4, 1608−1612

Cage like local structure of ionic liquids revealed by ^{129}Xe chemical shift

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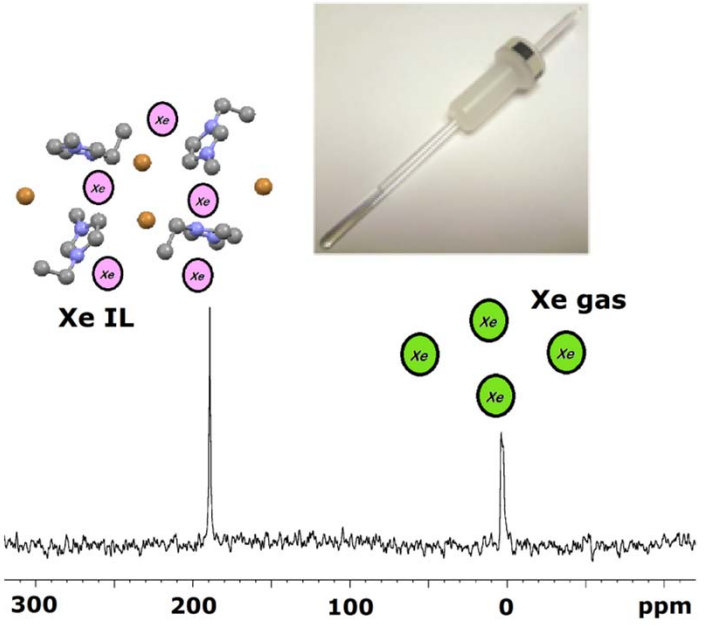
[a] Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, 20133 Milano, Italy.

[b] Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, 20125 Milano, Italy.

[c] CNR – Istituto di Chimica del Riconoscimento Molecolare, 20131 Milano, Italy.



J. Phys. Chem. Lett. **2013**, 4, 1608-1612

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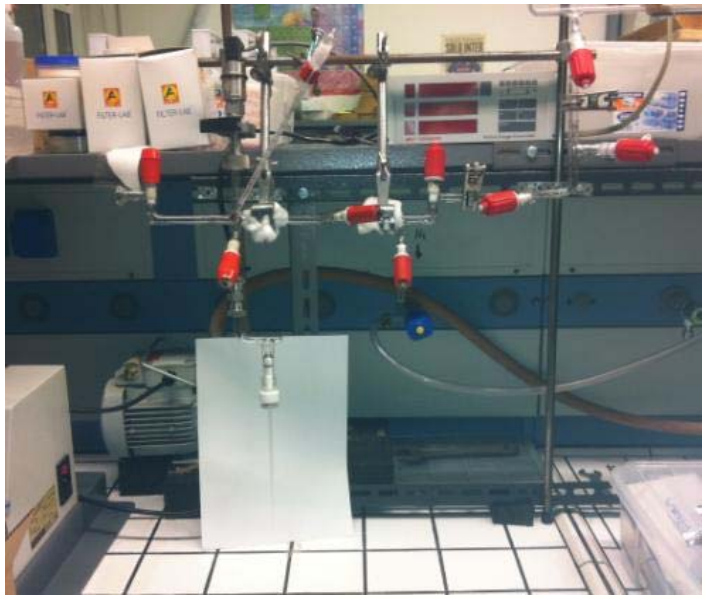
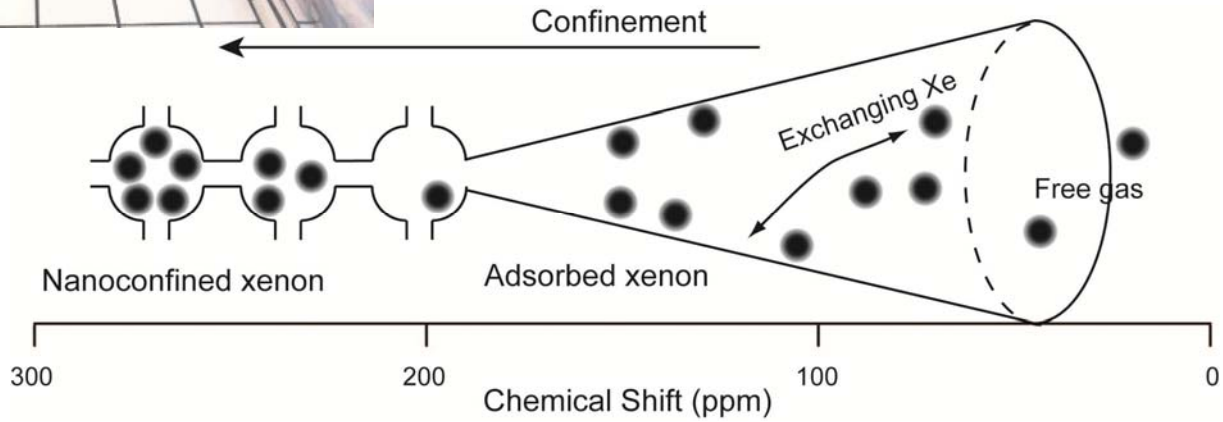
Methodology - ^{129}Xe NMR chemical shift

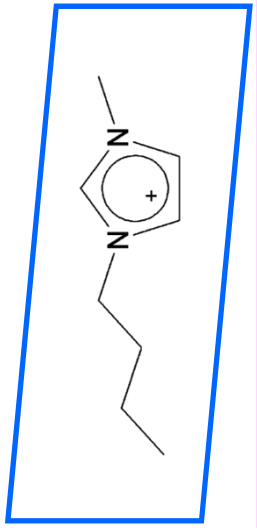
❖Experimental apparatus for Xenon loading in the NMR tube

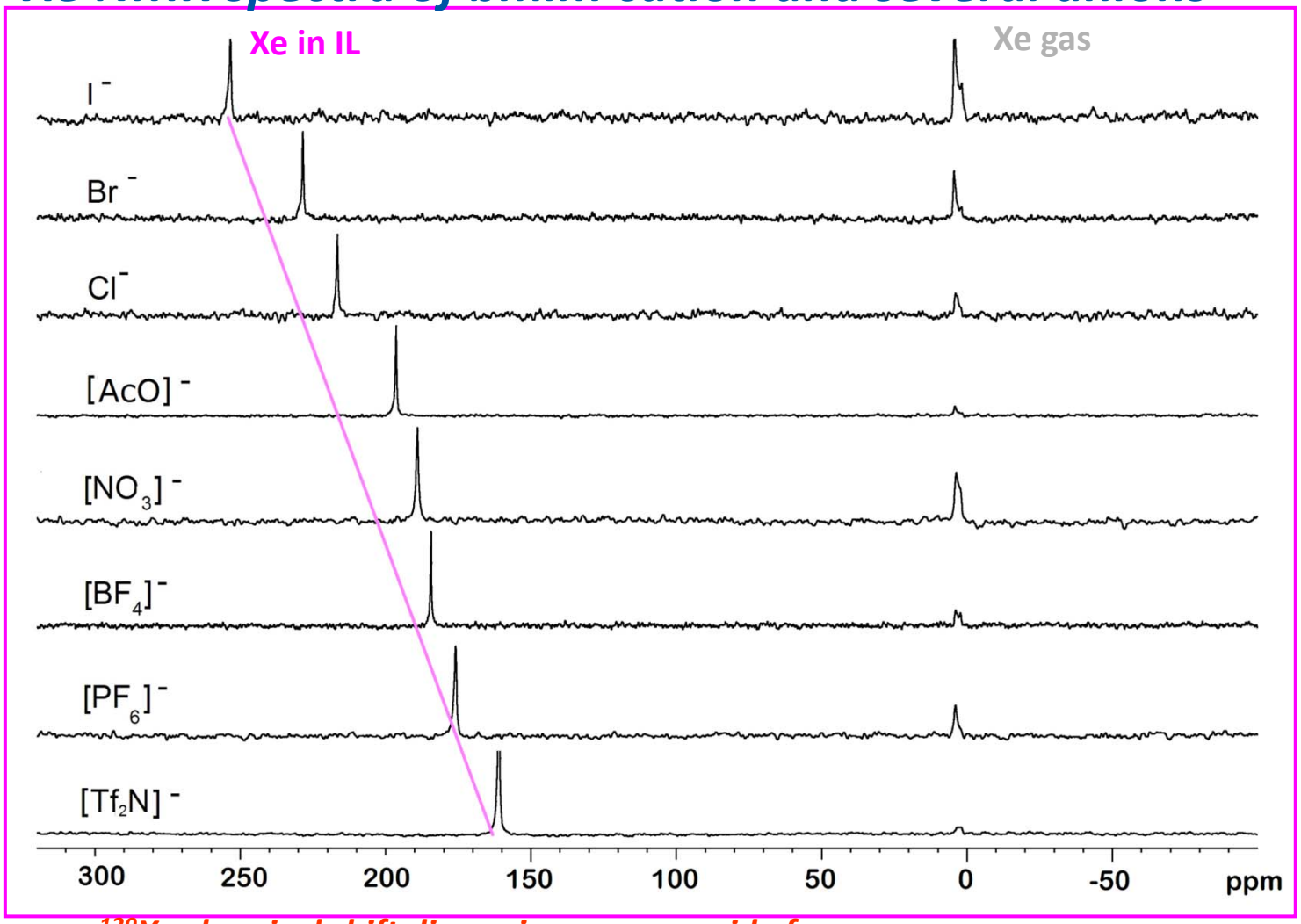




The ^{129}Xe shielding is influenced by the solvent cage dimensions

^{129}Xe NMR spectra of bmim cation and several anions





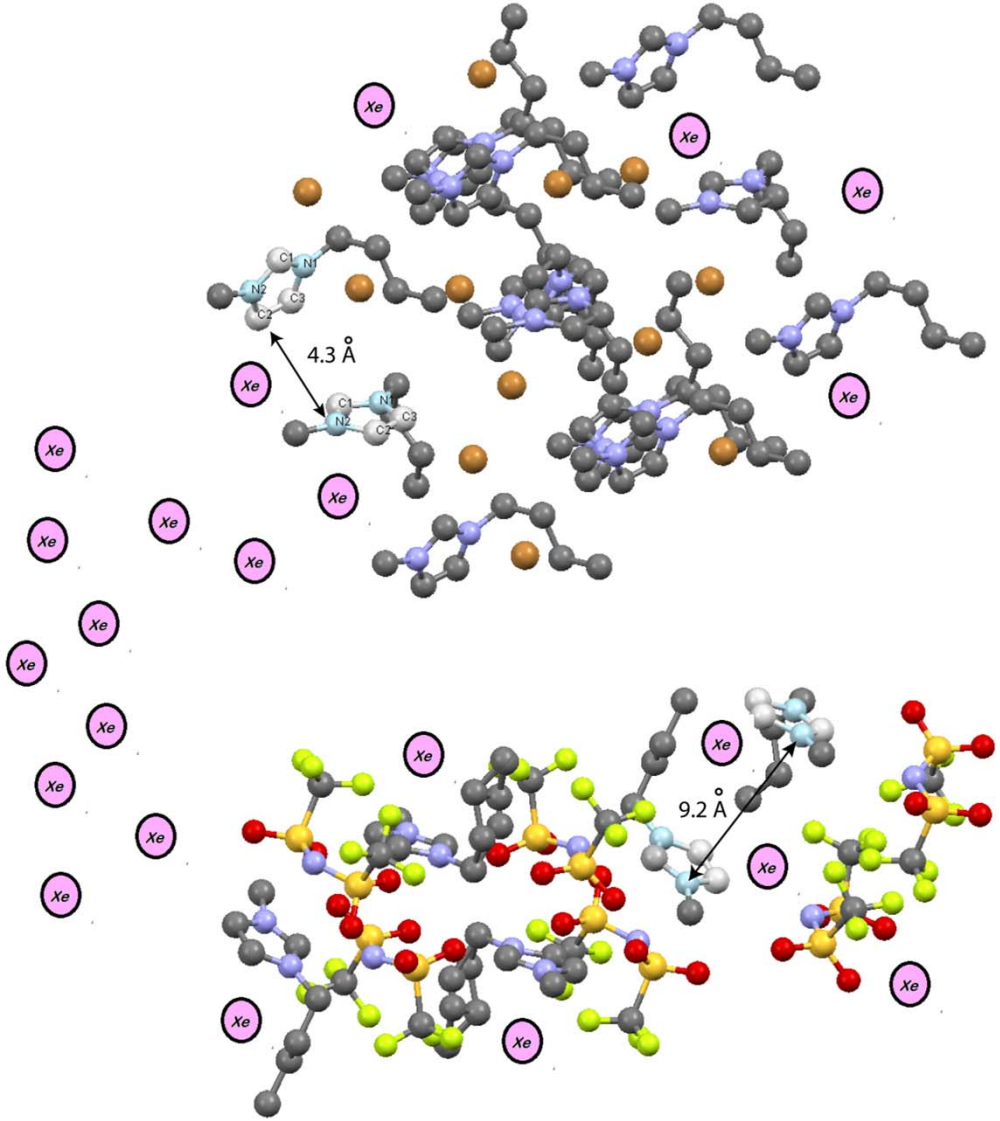
^{129}Xe chemical shift dispersion spans a wide frequency range.

$\Delta\delta$ of 100 ppm separates [bmim][I] from [bmim][Tf_2N].

Basic research: Local structure and dynamics

crystal structure of the ionic liquid
[bmim][Br]

Xenon gas seeking the IL voids



crystal structure of the ionic liquid
[bmim][Tf_2N^-]

Basic research: Local structure and dynamics

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Letter

pubs.acs.org/JPCL

Cage-Like Local Structure of Ionic Liquids Revealed by a ^{129}Xe Chemical Shift

Franca Castiglione,[†] Roberto Simonutti,[*,‡] Michele Mauri,[‡] and Andrea Mele[*,†,§]

[†]Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Piazza L. Da Vinci 32, 20133 Milano, Italy

[‡]Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, Via Roberto Cozzi 53, 20125 Milano, Italy

[§]CNR – Istituto di Chimica del Riconoscimento Molecolare, Via L. Mancinelli 7, 20131 Milano, Italy

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Letter

pubs.acs.org/JPCL

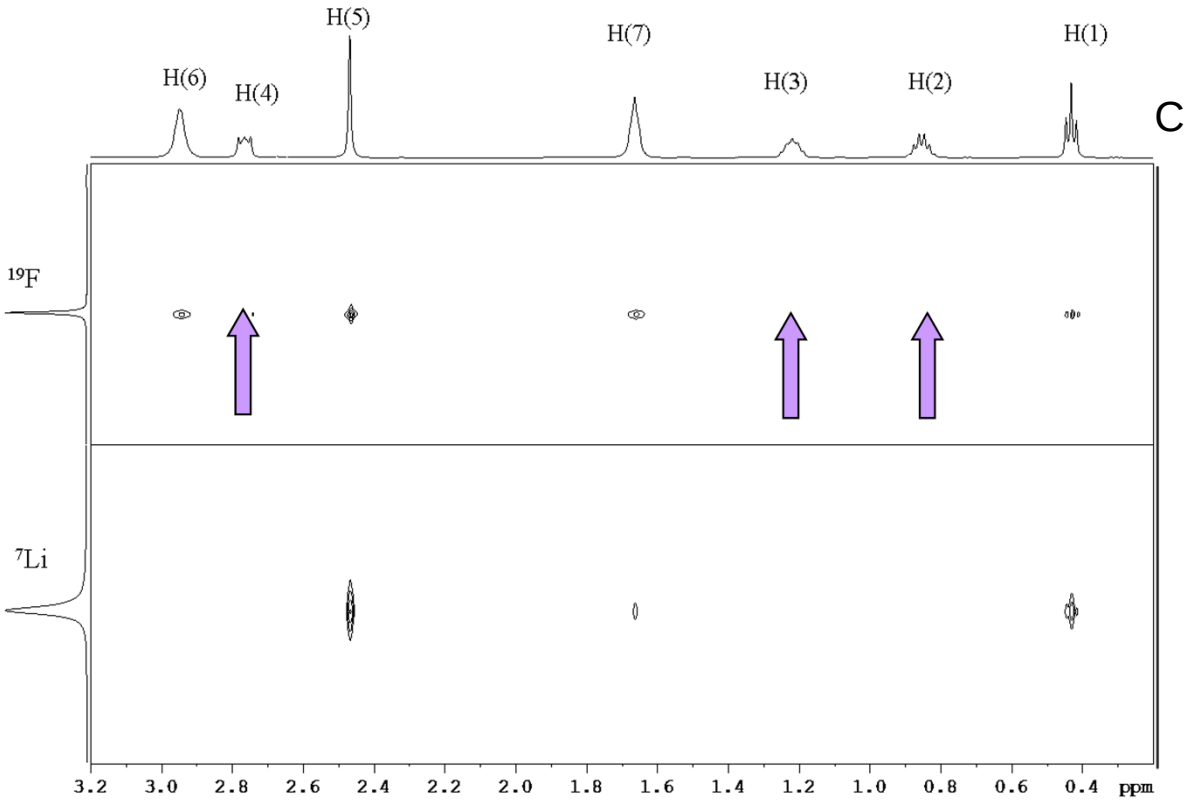
Using ^{129}Xe NMR to Probe the Structure of Ionic Liquids

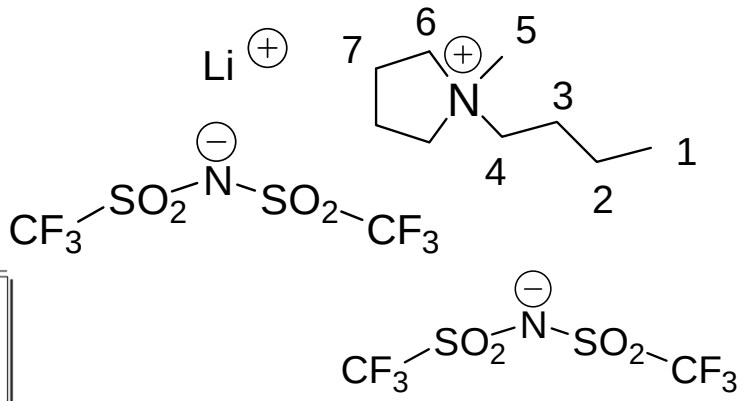
Pedro Morgado,[†] Karina Shimizu,[†] José M. S. S. Esperança,[‡] Patrícia M. Reis,[‡] Luís P. N. Rebelo,[‡] José N. Canongia Lopes,[*,†,‡] and Eduardo J. M. Filipe[*,†]

[†]Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal

[‡]Instituto de Tecnologia Química e Biológica (www.itqb.unl.pt), Universidade Nova de Lisboa, 2750-154 Oeiras, Portugal

1. New systems for LIB





Same type of selectivity observed for undoped $PYR_{14}TFSI$

Similar NOE pattern observed for Li^+ / PYR_{14}^+ interaction.

Puzzling result…

The components are close in space despite coulombic repulsion

F. Castiglione, M. Moreno, G. Raos, A. Famulari, A. Mele, G. B. Appetecchi, S. Passerini

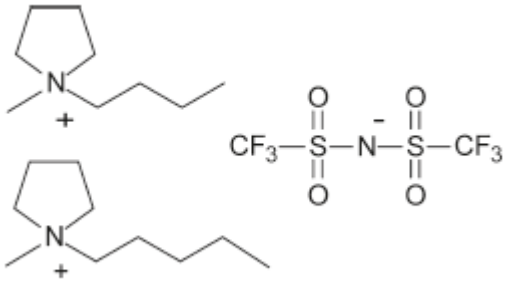
J. Phys. Chem. B **2009,** *113*, 10750.

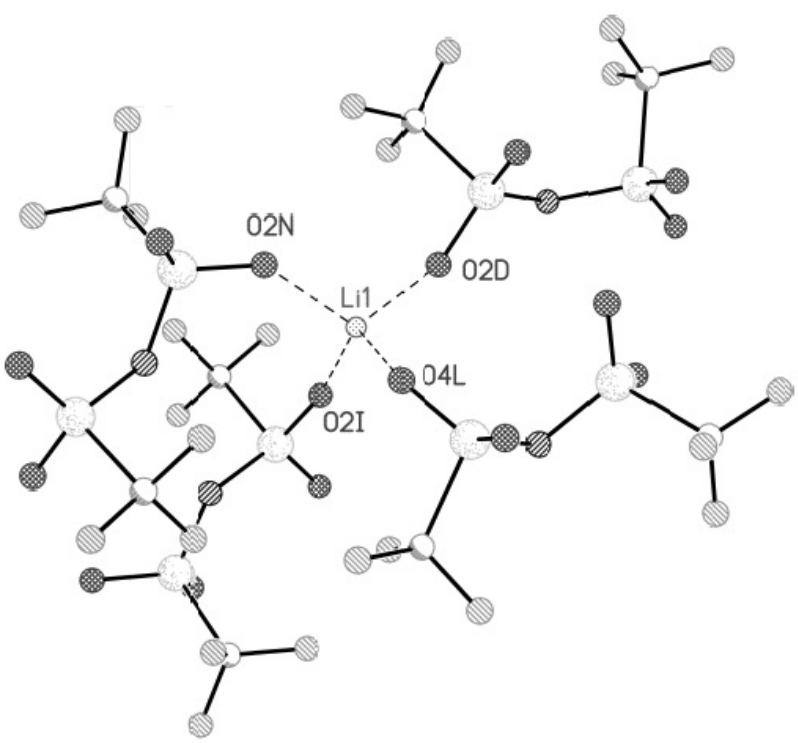
NOE evidence for strong coordination Li-TFSI

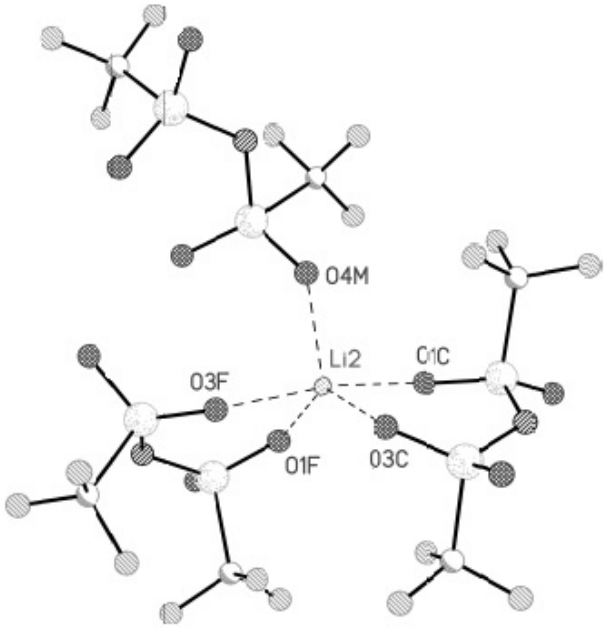
1. New systems for LIB

(1-x) $PYR_{1n}TFSI$-(x) LiTFSI

n = 4, 5; x=0.67







Q. Zhou, P. D. Boyle, L. Malpezzi, A. Mele, J.-H. Shind, S.Passerini, W. A. Henderson *Chem. Mater.* **2011**, *23*, 4331

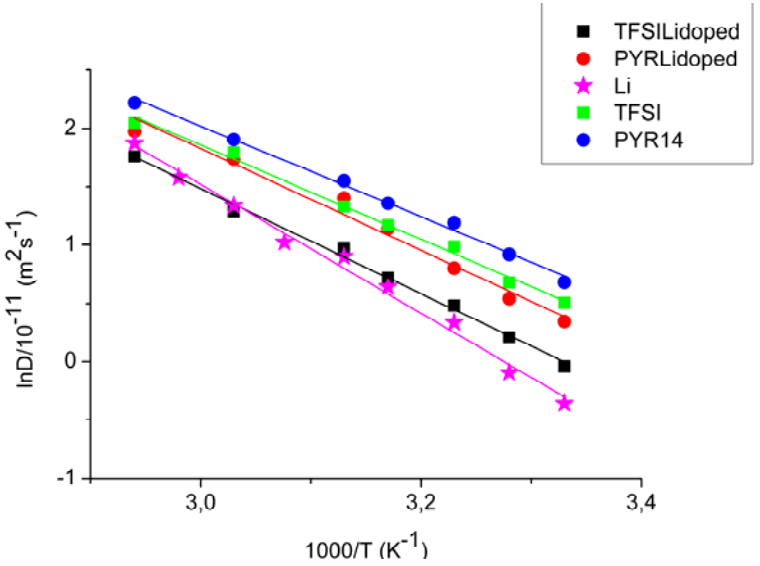
1. New systems for LIB

Experimental self-diffusion coefficients D (m^2s^{-1}) at 305 K, activation energy $E_a[D]$ (kJ/mol) for 0.1 LiTFSI – 0.9 $PYR_{14}TFSI$ and for pure $PYR_{14}TFSI$.

Ion	D_{sol}[a]	D_{pure}[b]	$E_a[D_{sol}]$[a]	$E_a[D_{pure}]$[b]
PYR_{14}^+	1.7×10^{-11}	2.5×10^{-11}	36	31
Li^+	0.91×10^{-11}	-	46	-
$TFSI^-$	1.23×10^{-11}	1.97×10^{-11}	37	31

[a] This work

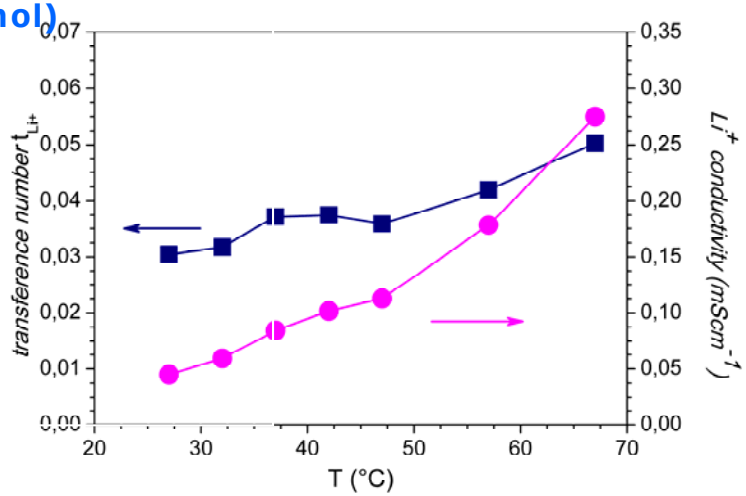
[b] From F. Castiglione et al. *J. Phys. Chem.* B **2009**, *113*, 10750.

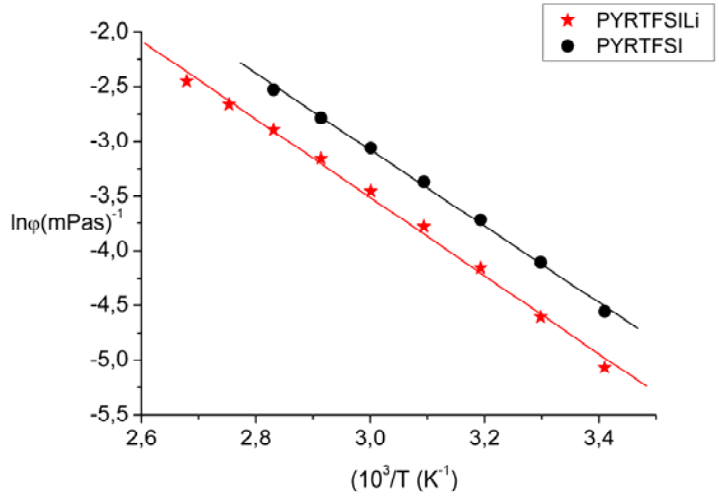


1.
$D(Li^+) < D(TFSI^-) < D(PYR_{14}^+)$
Consistent with $[Li(TFSI)_n]^{n-1}$

2.
The Ea(ϕ)= 30 (kJ/mol) for the Li-doped mixture *versus* 29 (kJ/mol) of the pure IL.

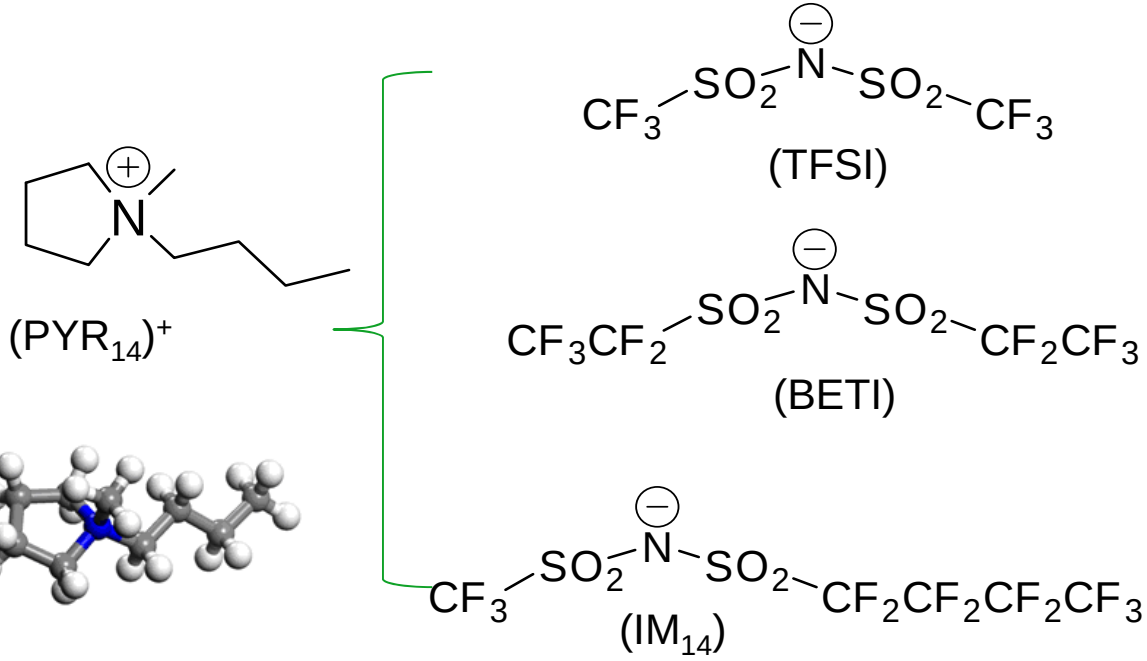
3.
Increased Li^+ conductivity



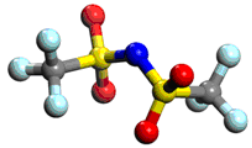


F. Castiglione, E. Ragg, A. Mele, G. B. Appetecchi, M. Montanino, S. Passerini, *J. Phys. Chem. Lett.*. **2011,** *2*, 153.

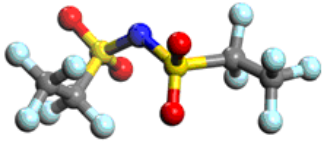
1. New systems for LIB



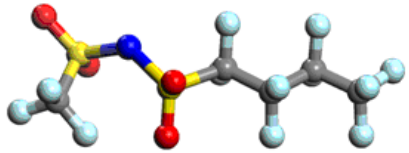
+ Li(TFSI) **1**



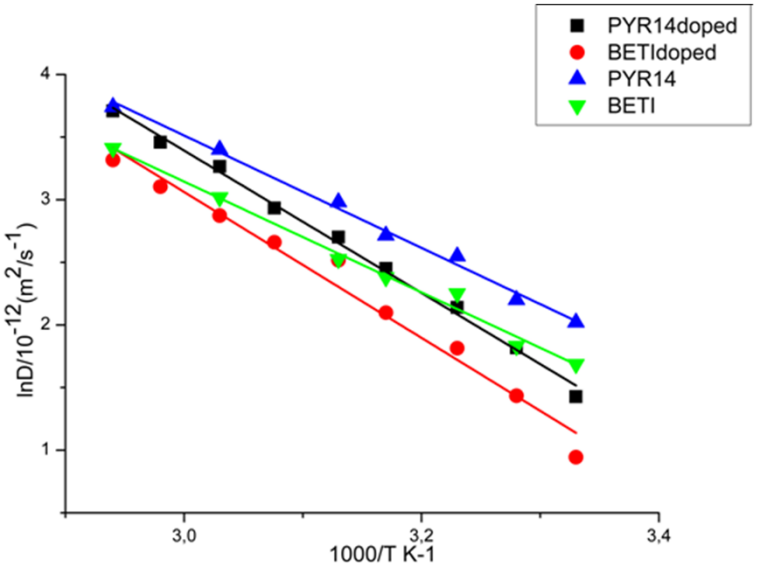
+ Li(BETI) **2**



+ Li(IM_{14}) **3**



1. New systems for LIB



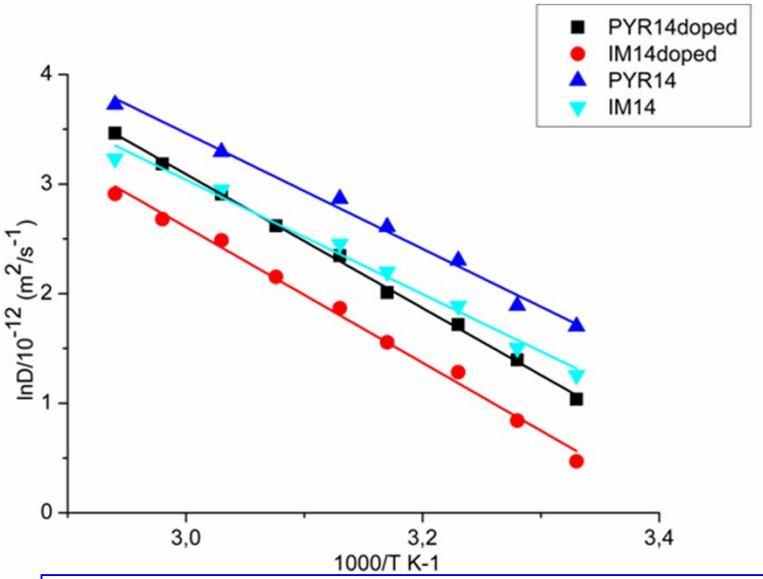
Ref.

$E_a(PYR_{14})_{puro}$ = 37 KJ/mol

$E_a(BETI)_{puro}$ = 37 KJ/mol

$E_a(PYR_{14})_{doped}$ = 46 KJ/mol

$E_a(BETI)_{doped}$ = 47 KJ/mol



Ref.

$E_a(PYR_{14})_{puro}$ = 43 KJ/mol

$E_a(IM_{14})_{puro}$ = 43 KJ/mol

$E_a(PYR_{14})_{doped}$ = 50 KJ/mol

$E_a(IM_{14})_{doped}$ = 49 KJ/mol

Ref.: F. Castiglione et al. *J. Phys. Chem. B* **2009,** *113,* 10750–10759

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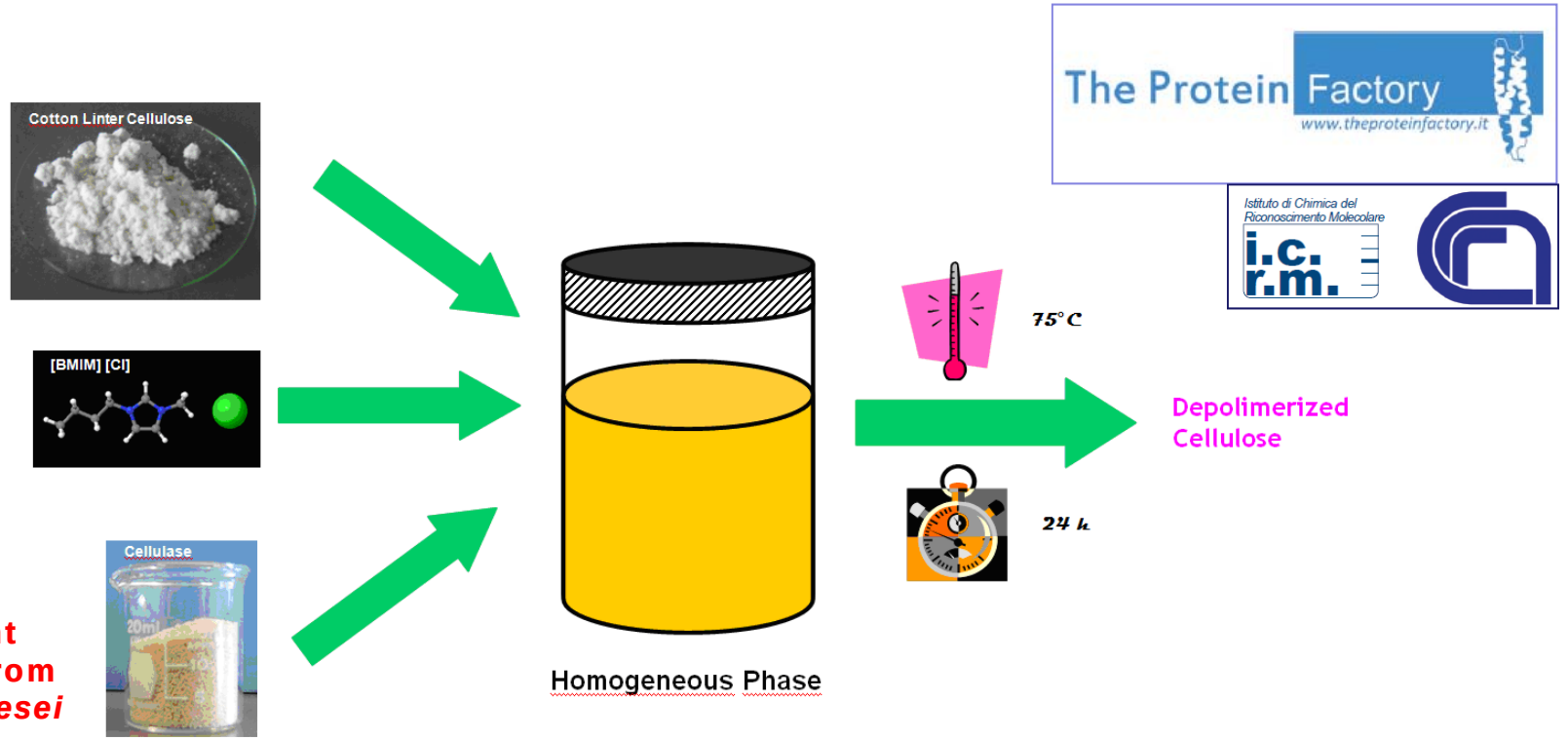
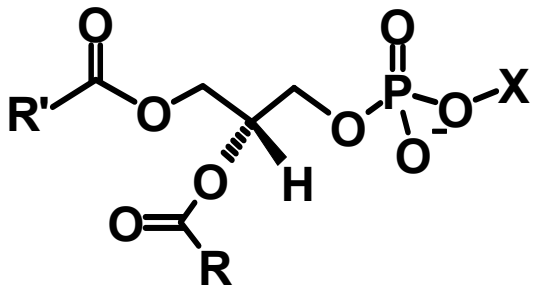
Single-batch, homogeneous phase enzyme-catalyzed depolymerization of cellulose in ionic liquid [BMIM][Cl]

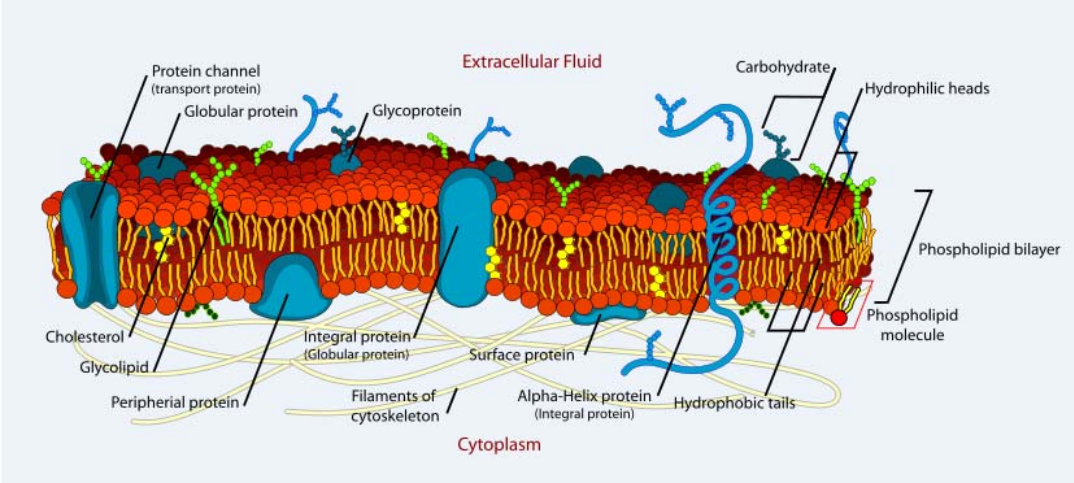
Paola D'Arrigo, Stefano Tamborini, Cristina Formantici, Yves Galante, Loredano Pollegioni, and Andrea Mele*
submitted



Action for COST: modeling of proteins in ILs

Phospholipids and ILs





OBJECTIVES:

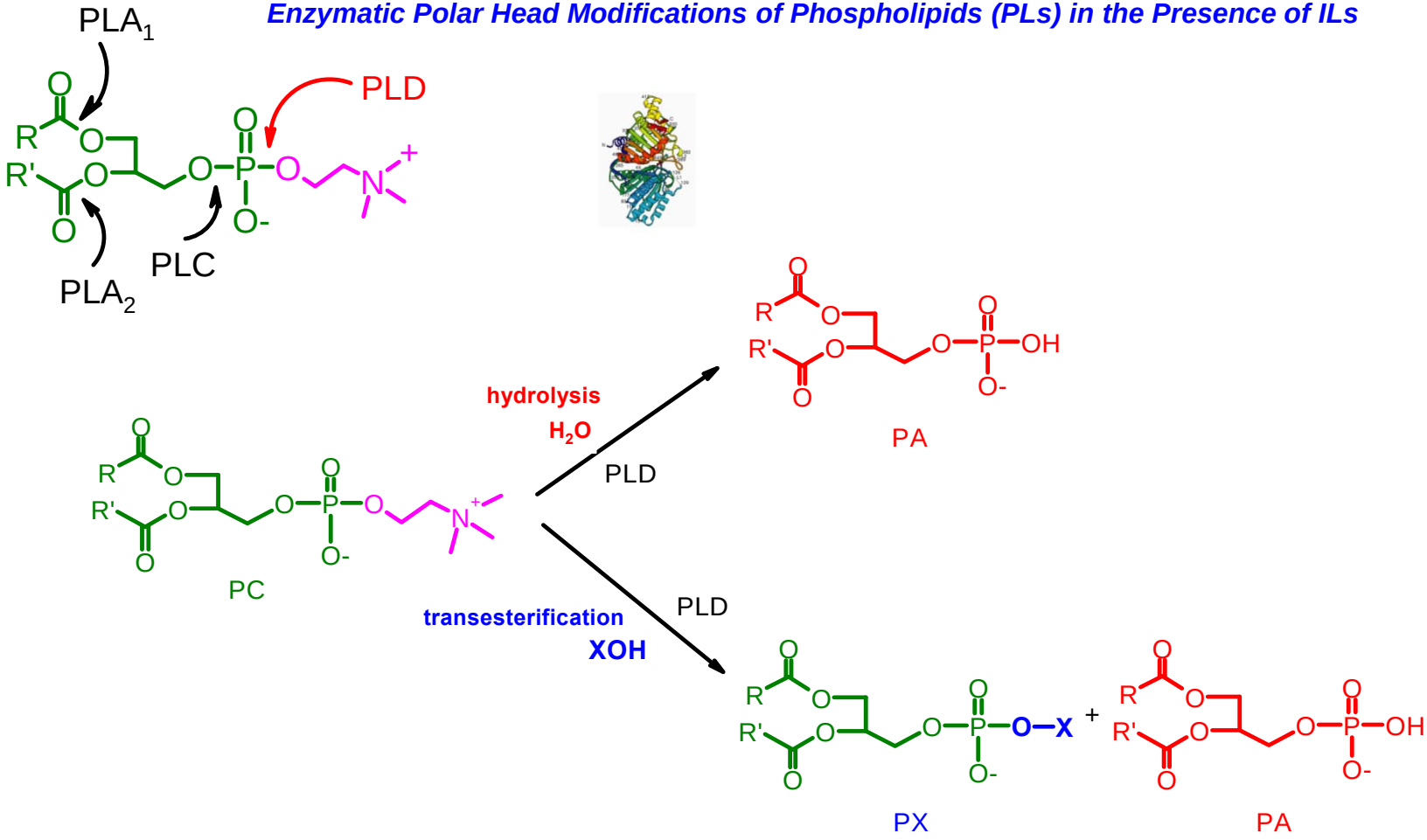
Evaluation of the solubility of the PLs and their aggregation in ILs

Study of phospholipases interactions with ILs (stability, activity and selectivity)

Utilization of ILs as solvents or co-solvents for PLs biotransformations

Set-up of a preparative synthesis of PLs of industrial interest using ILs

Enzymatic Polar Head Modifications of Phospholipids (PLs) in the Presence of ILs



PROBLEM: **difficult and expensive purification of the desired product (PX) from the by-product phosphatidic acid (PA).**

STRATEGY: **possible use of ILs to suppress hydrolytic activity of PLD**

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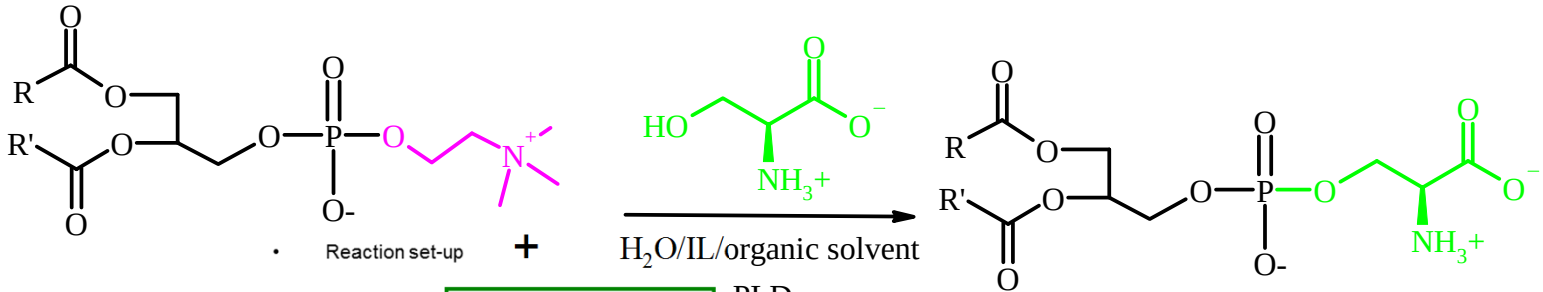
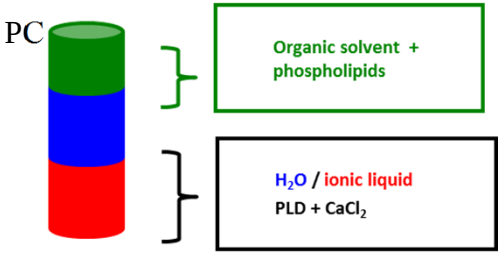
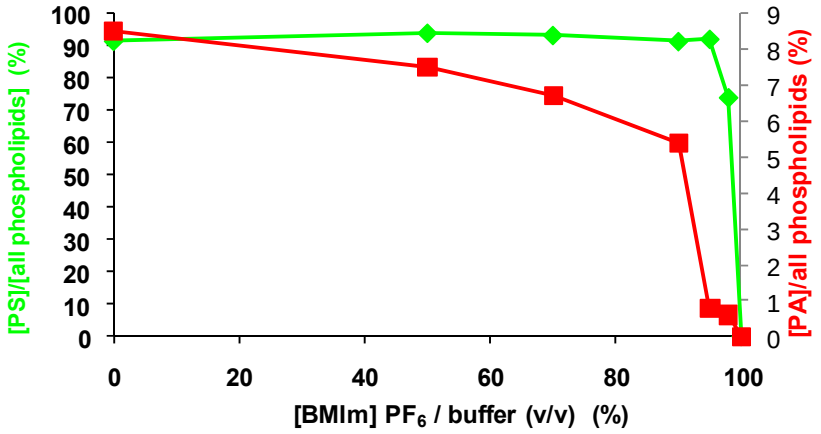
Synthesis of phosphatidylserine using [BMIm]PF_6 as a cosolvent





Importance of PS:

- Great commercial interest
- Present in cellular membranes expecially in brain
- Involved in many neurological processes
- Low levels of PS ⇒ memory problems, Alzheimer's disease, mental pathologies
- Assuming PS ⇒ mind and memory enhancement, reduction of age-related decline in mental function, reduction of depression, improvement of thinking skills also in youg people



With a Reaction medium: Toluene/ [BMIm]PF_6 :buffer (95:5)

- **Quantitative suppression of unwanted hydrolitic side-reaction([PA] ↓↓)**
- **High selectivity PS/PA >>**
- **easier purification**

P.D'Arrigo, L.Cerioli, C.Chiappe, W.Panzeri, D.Tessaro, A.Mele *J. Molecular Catalysis B* **2012**, 132-135.

New ILs: synthesis and characterization

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76 CHIMIA 2011, 65, No. 1/2 GLYCOCHEMISTRY TODAY
doi:10.2533/chimia.2011.76 Chimia 65 (2011) 76–80 © Schweizerische Chemische Gesellschaft

Sugar-Derived Ionic Liquids

Alberto Marra[a*], Cinzia Chiappe[b], and Andrea Mele[c]

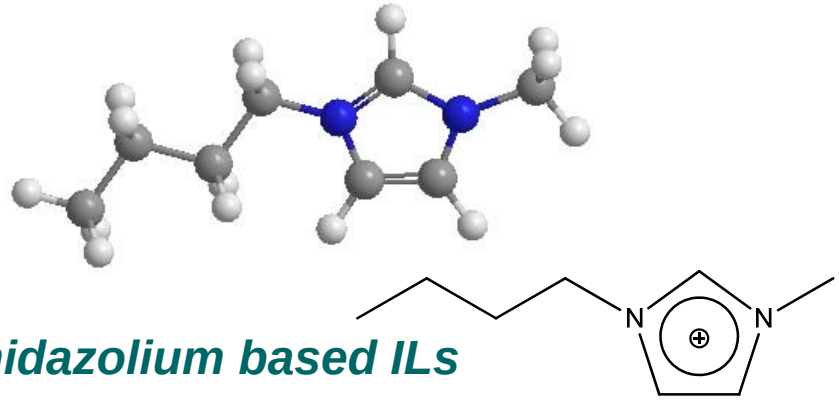
Top Curr Chem (2010) 295: 177–195
DOI: 10.1007/128_2010_47

Published online: 31 March 2010

Synthesis and Applications of Ionic Liquids Derived from Natural Sugars

Cinzia Chiappe, Alberto Marra, and Andrea Mele

New ILs: synthesis and characterization



Imidazolium based ILs

§ Wide liquid range

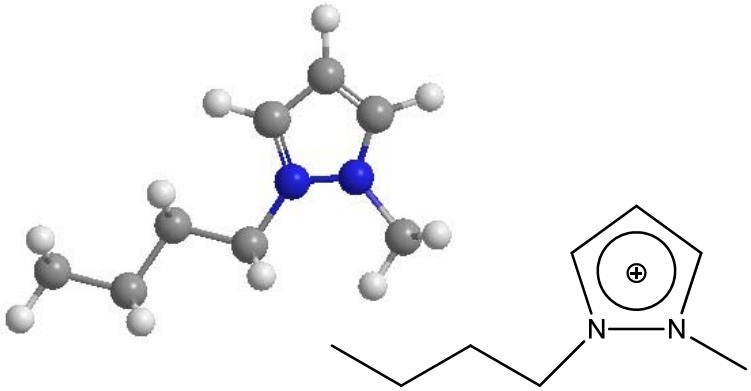
§ High conductivity

§ Reasonable viscosity

§ Possibility of tuning physico chemical properties:

- by varying the alkyl chain
- by changing the anion
- by chemical functionalization

§ In some cases structured domains are formed – heterogeneous structure at nm scale



Pyrazolium based ILs

§ Marginally investigated

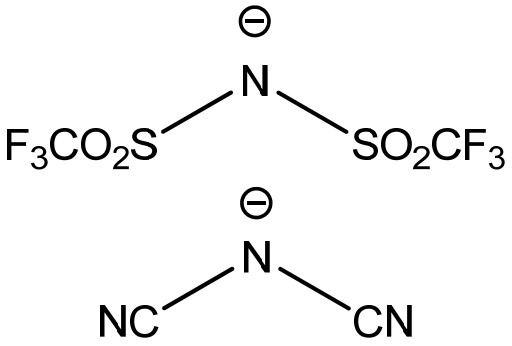
§ High conductivity

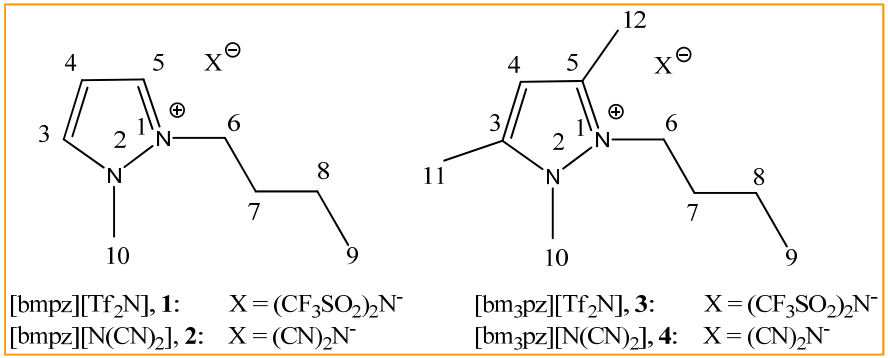
§ Low viscosity

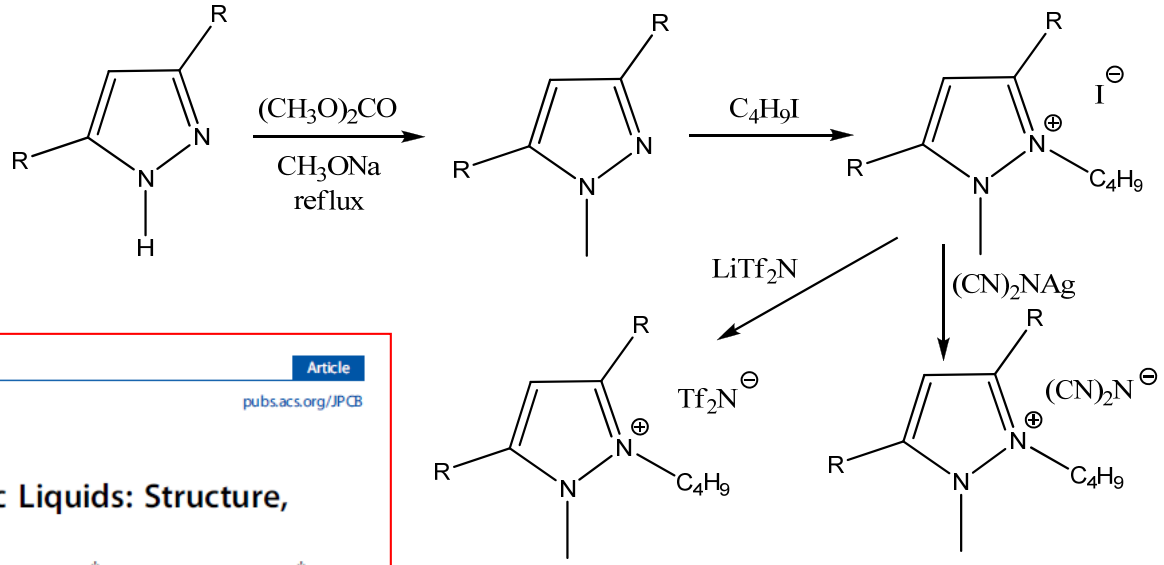
§ good EC properties

The different charge distribution may affect the nanostructuring (if any) of Pyz-based ILs

New ILs: synthesis and characterization







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Pyrazolium- versus Imidazolium-Based Ionic Liquids: Structure, Dynamics and Physicochemical Properties

Cinzia Chiappe,*,† Angelo Sanzone,† Daniele Mendola,‡ Franca Castiglione,‡ Antonino Famulari,‡ Guido Raos,‡ and Andrea Mele*,‡,§

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