Experimental report

13/02/2017

Proposal: **6-02-531** **Council:** 4/2014

Title: Dynamics of ionic liquids under confinement

Research area: Soft condensed matter

This proposal is a continuation of 6-02-523

Main proposer: **Filippo FERDEGHINI**

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Local contacts: Orsolya CZAKKEL

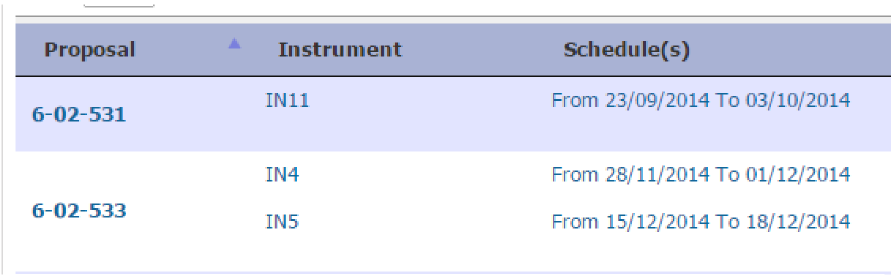
Samples: Al203
C12H23BF4N2

Instrument	Requested days	Allocated days	From	To
IN5	5	0		
IN11	10	10	23/09/2014	03/10/2014

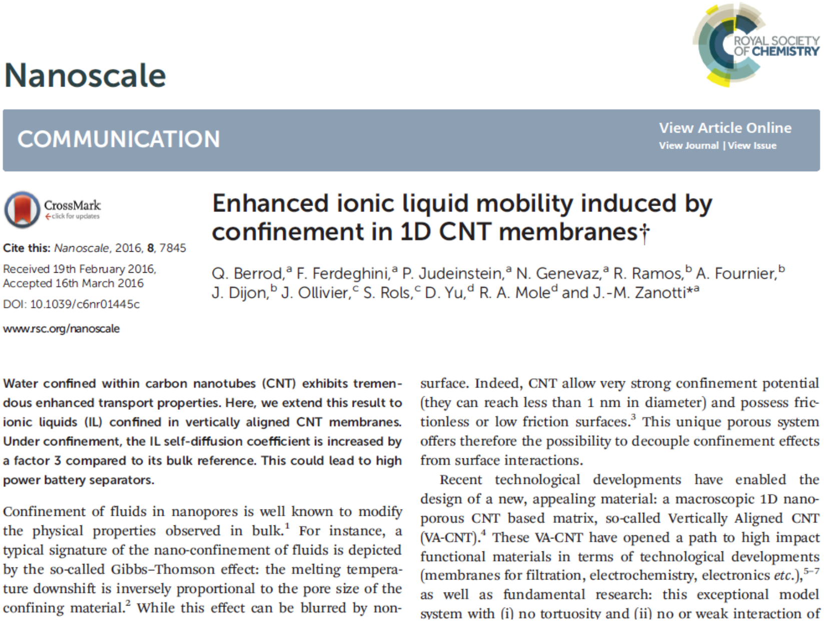
Abstract:

The propensity of Ionic Liquids (IL) to self-organize in transient nanoscopic domains induces a low ionic conductivity at long time (ms) and large scale (micrometer). We propose to lift the detrimental effect by frustrating the formation of the IL nanometric domains using confinement of the IL within a controlled porous structure. While a prepeak around 0.2-0.4 Å-1 of the confined IL structure factor can be used to quantify (in situ and on line) the extent of the nanosegregation, we will focus on the measurement of the translational self-diffusion coefficient of the center-of-mass of the confined IL molecules. The parasitic quasi-elastic contribution(s) of the IL side-chains will be discarded by use of a specifically deuterated IL.

Experimental Reports



Proposal	Instrument	Schedule(s)
6-02-531	IN11	From 23/09/2014 To 03/10/2014
6-02-533	IN4	From 28/11/2014 To 01/12/2014
	IN5	From 15/12/2014 To 18/12/2014



Nanoscale

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Cite this: *Nanoscale*, 2016, **8**, 7845

Received 19th February 2016, Accepted 16th March 2016

DOI: 10.1039/c6nr01445c

www.rsc.org/nanoscale

Enhanced ionic liquid mobility induced by confinement in 1D CNT membranes†

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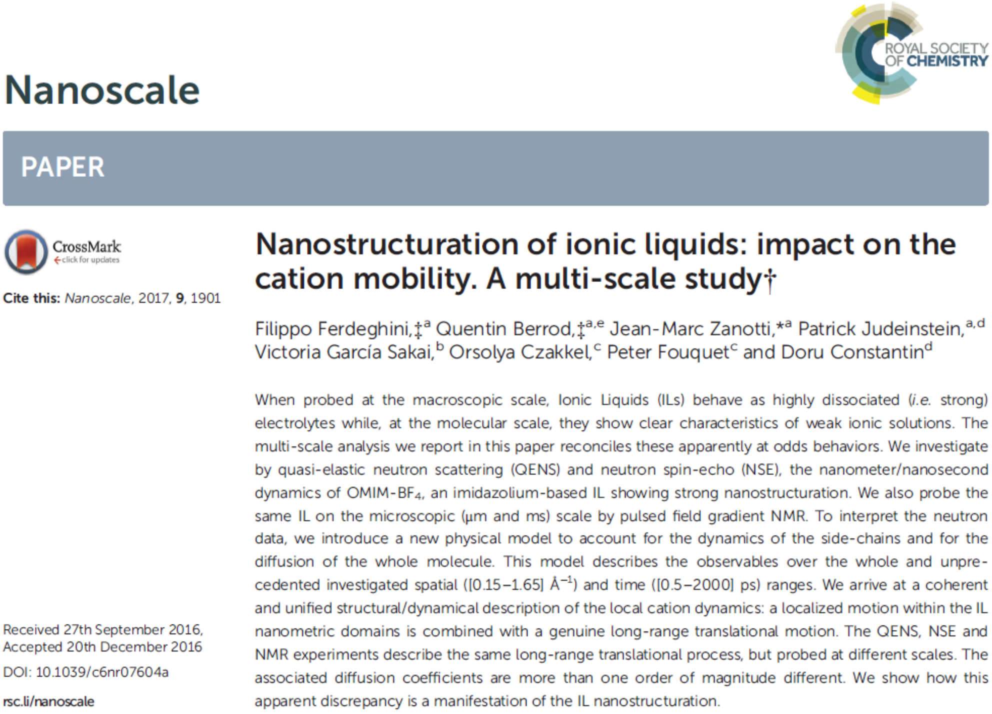
Water confined within carbon nanotubes (CNT) exhibits tremendous enhanced transport properties. Here, we extend this result to ionic liquids (IL) confined in vertically aligned CNT membranes. Under confinement, the IL self-diffusion coefficient is increased by a factor 3 compared to its bulk reference. This could lead to high power battery separators.

Confinement of fluids in nanopores is well known to modify the physical properties observed in bulk.[1] For instance, a typical signature of the nano-confinement of fluids is depicted by the so-called Gibbs–Thomson effect: the melting temperature downshift is inversely proportional to the pore size of the confining material.[2] While this effect can be blurred by non-surface. Indeed, CNT allow very strong confinement potential (they can reach less than 1 nm in diameter) and possess frictionless or low friction surfaces.[3] This unique porous system offers therefore the possibility to decouple confinement effects from surface interactions.

Recent technological developments have enabled the design of a new, appealing material: a macroscopic 1D nanoporous CNT based matrix, so-called Vertically Aligned CNT (VA-CNT).[4] These VA-CNT have opened a path to high impact functional materials in terms of technological developments (membranes for filtration, electrochemistry, electronics *etc.*),[5–7] as well as fundamental research: this exceptional model system with (i) no tortuosity and (ii) no or weak interaction of



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Cite this: *Nanoscale*, 2017, **9**, 1901

Nanostructuration of ionic liquids: impact on the cation mobility. A multi-scale study†

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Received 27th September 2016, Accepted 20th December 2016

DOI: 10.1039/c6nr07604a

rsc.li/nanoscale

When probed at the macroscopic scale, Ionic Liquids (ILs) behave as highly dissociated (*i.e.* strong) electrolytes while, at the molecular scale, they show clear characteristics of weak ionic solutions. The multi-scale analysis we report in this paper reconciles these apparently at odds behaviors. We investigate by quasi-elastic neutron scattering (QENS) and neutron spin-echo (NSE), the nanometer/nanosecond dynamics of OMIM-BF$_4$, an imidazolium-based IL showing strong nanostructuration. We also probe the same IL on the microscopic (μm and ms) scale by pulsed field gradient NMR. To interpret the neutron data, we introduce a new physical model to account for the dynamics of the side-chains and for the diffusion of the whole molecule. This model describes the observables over the whole and unprecedented investigated spatial ([0.15–1.65] Å^{-1}) and time ([0.5–2000] ps) ranges. We arrive at a coherent and unified structural/dynamical description of the local cation dynamics: a localized motion within the IL nanometric domains is combined with a genuine long-range translational motion. The QENS, NSE and NMR experiments describe the same long-range translational process, but probed at different scales. The associated diffusion coefficients are more than one order of magnitude different. We show how this apparent discrepancy is a manifestation of the IL nanostructuration.