Supporting Information

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

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CNT forest synthesis and characterization:

CNT forests were grown on alumina-covered silicon wafers using iron as a catalyst (1 nm Fe on 10 nm Al_2O_3). Hot filament assisted chemical vapor deposition with acetylene carbon precursor was performed to grow 100 to 300 µm high CNT forests (Figure S1). The structure of the CNTs (diameter and number of walls) was analyzed by Transmission Electron Microscopy (TEM Tecnai Osiris operating at 200 kV) and was uniform from the base to the top of the forest. The CNT forest is mostly composed of small diameter multiwall CNT with 2 or 3 walls (80% of the population with 2 or 3 walls); with a median external diameter ~ 5.1 nm (standard deviation ~ 1.1 nm) and median internal diameter ~ 4 nm (Figure S1). A surfacic density of ~3.10^{11} CNT/cm^2 was estimated using the liquid-induced compaction technique.

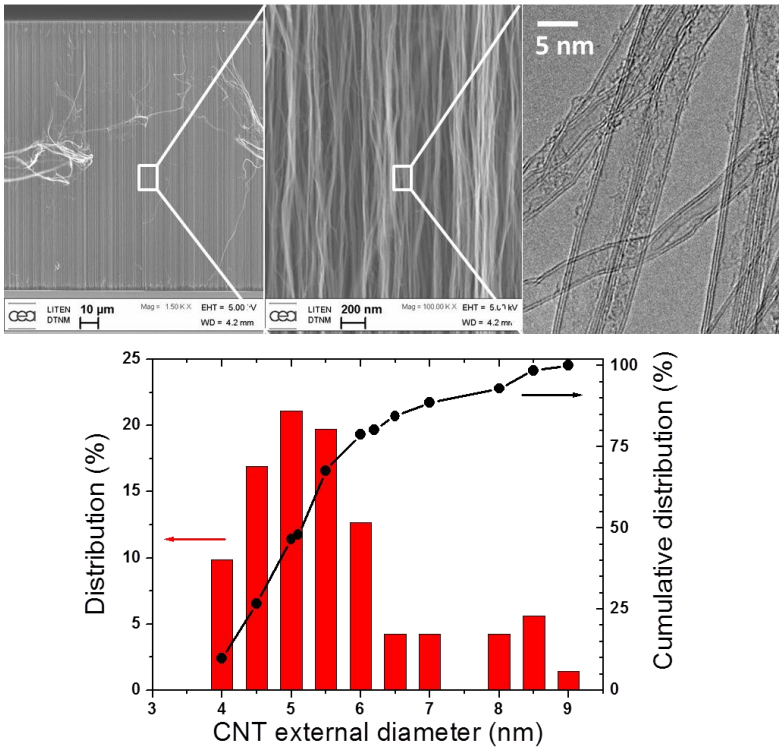

Figure S1. (top) SEM and TEM images of CNT forest grown on silicon wafers; (bottom) External CNT diameter distribution.

CNT membranes characterization

The presence of polystyrene over the whole thickness of the CNT membrane has been checked with SEM images and confocal Raman spectroscopy at 633 nm laser excitation (Figure S2). The measurements have been performed on the cross-section of the CNT membrane. The Raman signature of polystyrene is observed over the whole thickness, showing that the CNT forest is well filled with the polymer.

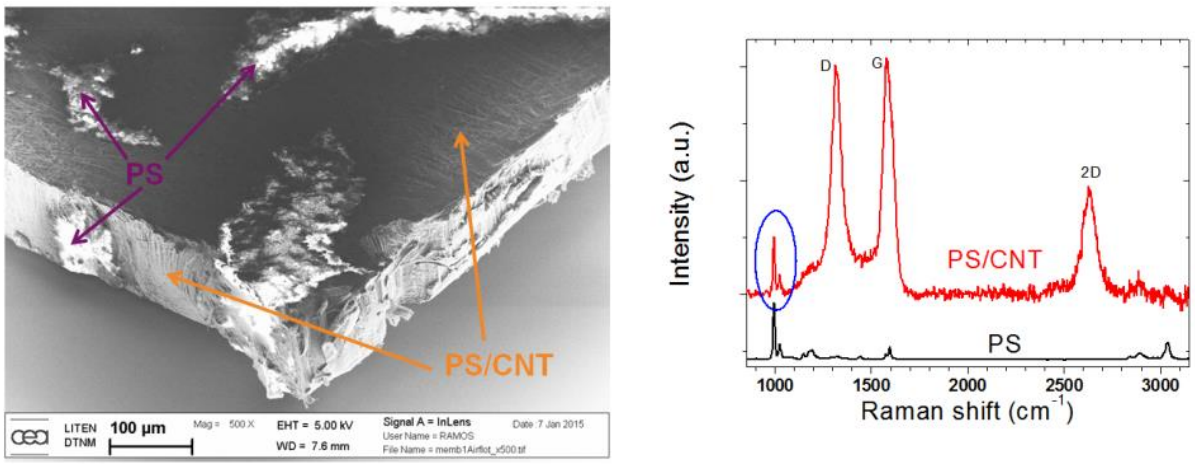

Figure S2. a) SEM image of the CNT membrane. b) Raman spectra recorded on the cross-section of the CNT membrane: the Raman signature of polystyrene is observed over the whole thickness.

PFG-NMR measurements:

NMR experiments were performed on a Bruker NMR spectrometer equipped with a z-axis gradient. NMR resonance frequencies for ^{1}H, and ^{19}F nuclei were respectively 400.13 and 376.50 MHz. The self-diffusion coefficient, D_S, was determined according to the equation:

$$A(g)/A(0) = \exp\left(-\gamma^2 g^2 \delta^2 D_S(\Delta - \delta/3)\right)$$

where A, γ, g, δ and Δ stand for the signal areas, the gyromagnetic ratio of the investigated nucleus, the intensity of the magnetic field gradient, the duration of the gradient pulse and the diffusion time respectively. The magnitude of the pulsed field gradient was varied as $0 \leq g \leq 1000$ G/cm; δ was set between 1 ms and 3 ms, depending on the diffusion coefficient of the mobile species. Δ was set between 10 ms and 50 ms for bulk IL. In the case of the confined IL the relaxation times (T_1) is shorter than in bulk and the NMR signal is drastically reduced for Delta = 50 ms. Therefore, for confined IL Ds values are given for Delta = 10 ms (and the maximum field gradient : 1000 G/cm).

QENS measurements:

Quasielastic neutron scattering (QENS) measurements have been performed on two time-of-flight (ToF) spectrometers:

- IN5 (at the Institut Laue Langevin, Grenoble France) using an incoming wavelength of 8Å, yielding a 20 μeV resolution and a [0.2 – 1.2 $Å^{-1}$] Q-range (Q being the momentum transfer).

- Pelican (at the Bragg Institute (ANSTO), Sydney Australia) using an incoming wavelength of 6Å, yielding a 70 μeV resolution and a [0.4 – 1.8 $Å^{-1}$] Q-range.

Samples were enclosed in a specifically designed Aluminum flat container (sealed with indium join) to probe the ionic liquids dynamics parallel or perpendicular to the CNT. The recorded S(θ,t) data, where t and θ stand for the time-of-flight and the scattering angle respectively, have been transformed into S(Q,ω) spectra, where ω is the energy transfer, using the Lamp software. A flat

piece of Vanadium has been used to measure the resolution function and correct the S(Q,ω) spectra from the detectors efficiency.

Figure S3 explains how to probe the proton dynamics along or perpendicular to the tubes. Indeed, during a QENS experiment, the dynamics is probed alongside the Q-vector. On Pelican (IN5), several orientations of the sample container have been selected from 99 to 135° (from 105 to 145°) yielding $Q_{//}$ ranging from 0.3 to 1.5 $Å^{-1}$ (0.4 to 1.3 $Å^{-1}$).

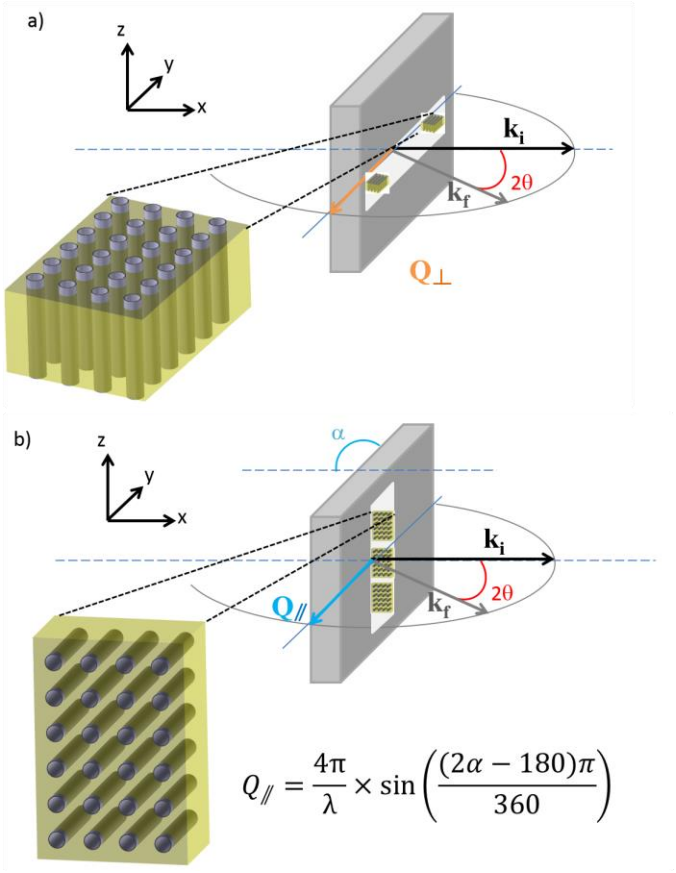

Figure S3. Schematic representation of the sample container for QENS experiment. a) In such orientation of the sample container, Q is perpendicular to the CNT for all 2θ values (in the xy plan). b) By rotating the sample container of 90°, Q is parallel to the CNT in one detector position. By rotating the sample container along z axis, several $Q_{//}$ can be obtained, following the equation shown in the figure.

The QENS spectra measured on Pelican in both directions are shown in Figure S3 and compared to the bulk reference. The dynamical structure factors are very similar in all cases. This result is in good agreement with ToF measurements performed on IN5 (Figure 3): under confinement there is no modifications of the $OmimBF_4$ local dynamics.

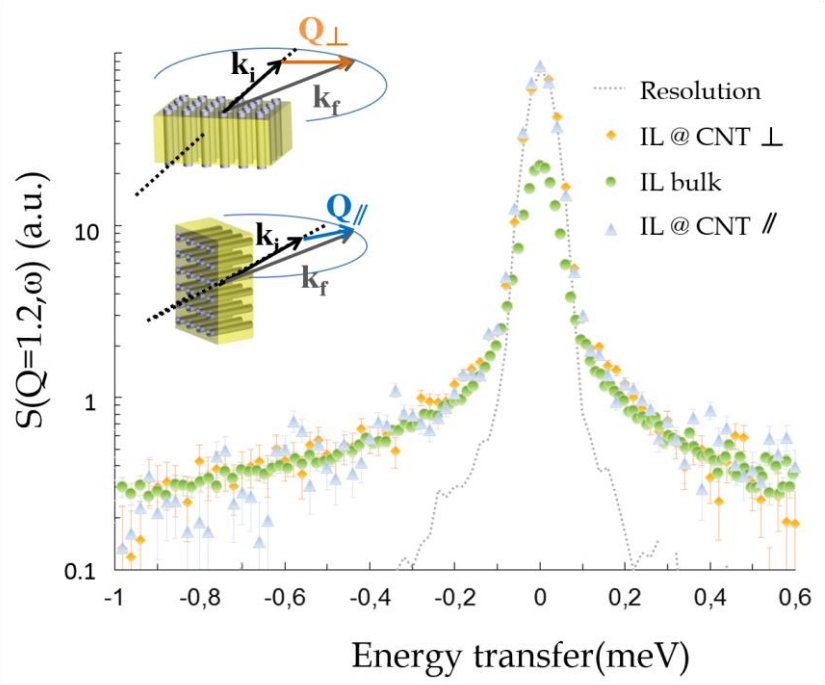

Figure S4. S(Q,ω) spectra (measured on Pelican-ANSTO) of bulk $OmimBF_4$ (green), and confined $OmimBF_4$ in the CNT membrane at Q = 1.2 $Å^{-1}$. The sample has been selectively oriented to probe the dynamics along (blue) or perpendicular (orange) to the CNT (see inset). The dotted line is the resolution function (70 μeV width).

The Q dependence of the S(Q,ω) spectra (measured on IN5) are shown in Figure S5 to highlight the similarity of the quasielastic signals (bulk IL, and confined IL in both orientations) over the whole Q-range (see Figure 3 for S(Q = 1, ω) spectra).

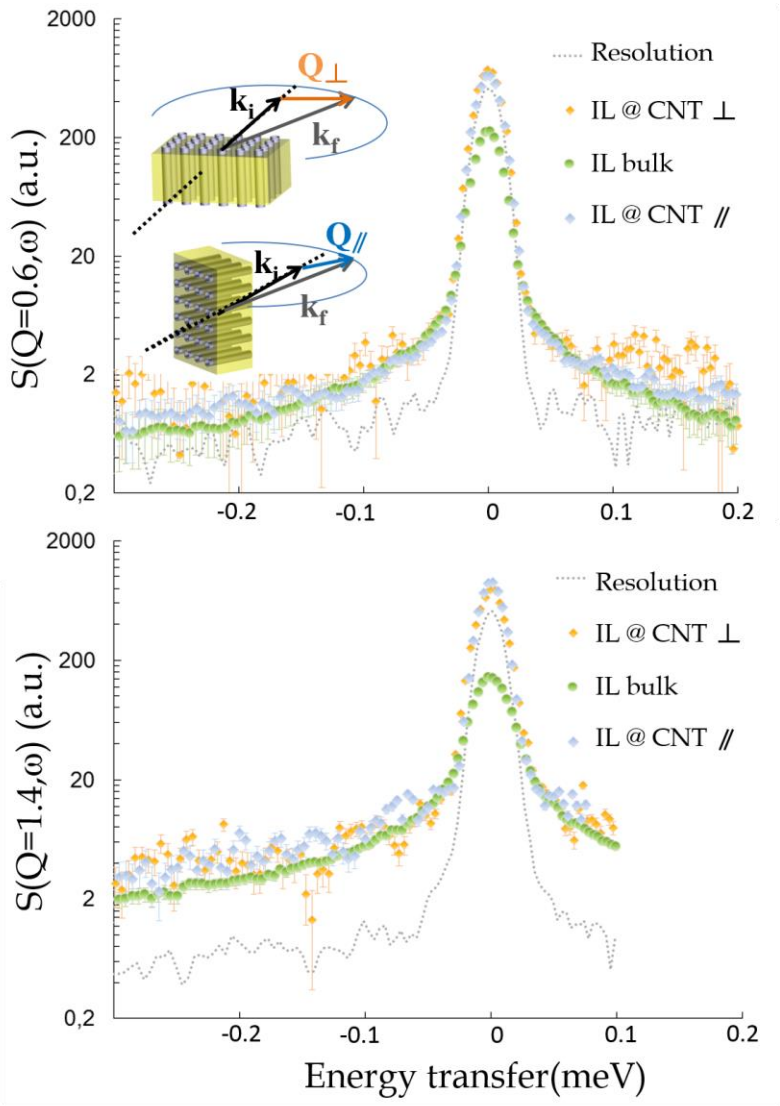

Figure S5. S(Q,ω) spectra (measured on IN5-ILL) of bulk $OmimBF_4$ (green), and confined $OmimBF_4$ in the CNT membrane at Q = 0.6 $Å^{-1}$(top) and Q = 1.4 $Å^{-1}$ (bottom). The sample has been selectively oriented to probe the dynamics along (blue) or perpendicular (orange) to the CNT (see inset). The dotted line is the resolution function (20 μeV width).