

## Supplementary information

# Ion conductive behaviour in a confined nanostructure: NMR observation of self-diffusion in a liquid-crystalline bicontinuous cubic phase

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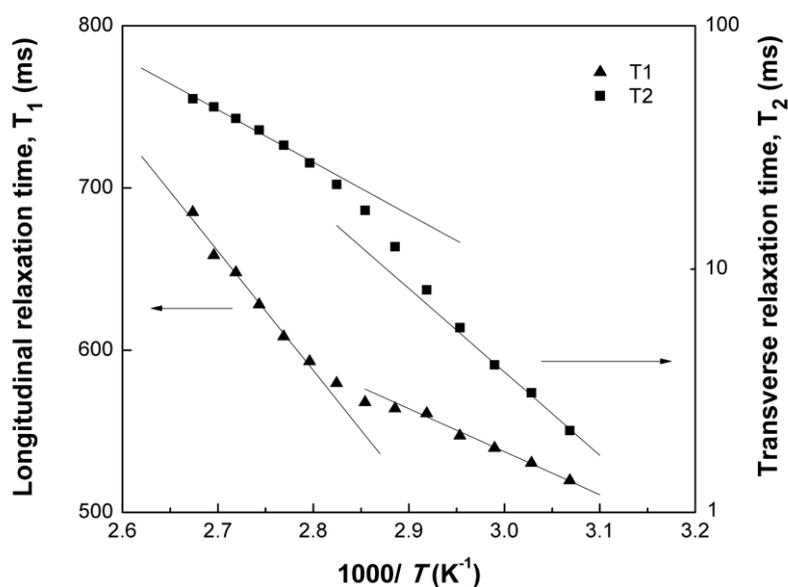
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**Experimental procedures.** Compound 1 displayed in Fig. 1 was synthesized according to the scheme in reference 1. The phases of the material were visually observed by an Olympus BH-2 optical polarizing microscope equipped with a Mettler FP82 HT hot-stage. Phase transition temperatures were determined by differential scanning calorimetry using a Netzsch DSC204 *Phoenix*®. A small amount of sample was sealed in an aluminium container and measurements were conducted under nitrogen atmosphere in a temperature interval spanning from -40 °C to 110 °C and at a heating rate of 10 °C/min. No birefringence in the liquid-crystalline bicontinuous cubic phase as well as the existence of phase transitions on cooling and heating were in excellent agreement with previous observations.

The preparations prior to the PFG-NMR measurements were as follows. The 90° pulse lengths were determined for proton (13 μs) and fluorine (15 μs). The longitudinal relaxation times ( $T_1$ ) and the transverse relaxation times ( $T_2$ ) were measured over the whole temperature range by inversion recovery and spin echo experiments, respectively. The recycle delay between individual scans (D1) was always set to more than  $5 * T_1$ . To improve the signal to noise ratio a Longitudinal Eddy-current Delay (LED)<sup>2</sup> pulse sequence was added after the stimulated-echo in the case of very short  $T_2$  (i.e. below 2 ms). The double stimulated-echo<sup>3</sup> pulse sequence was employed for the highest temperatures to diminish artefacts from convection. Bipolar pulses<sup>4</sup> were used in the proton measurements to remove the artefact due to cross-cross relaxation between different nuclei. The nominal values for all diffusion coefficients were calibrated towards the diffusion of water<sup>5</sup>,  $D = 2.3 * 10^{-9} \text{ m}^2 / \text{ s}$  at 298 K.

**Table S1.** Extreme values for  $T_1$  and  $T_2$  in the NMR relaxation measurements.

Nucleus	$T_1$ (ms)		$T_2$ (ms)	
	max.	min.	max.	min.
$^1\text{H}$	685.1	519.7	50.1	2.2
$^{19}\text{F}$	681.5	438.3	161.3	1.1



**Fig. S1** Temperature dependence of the longitudinal ( $T_1$ ) and transverse ( $T_2$ ) relaxation times of the cation signal. The solid lines are linear fits to the data points.

### Measurements of longitudinal and transverse relaxation times

A marked change in the relaxation times can be observed at around  $1000/T = 2.9$ . The temperature trends in  $T_1$  and  $T_2$  continue to change over a rather broad temperature region up to approximately  $1000/T = 2.8$ . We assume this behaviour is due to the gradual decrease of order in the bicontinuous cubic phase at the temperature range near the isotropization point.

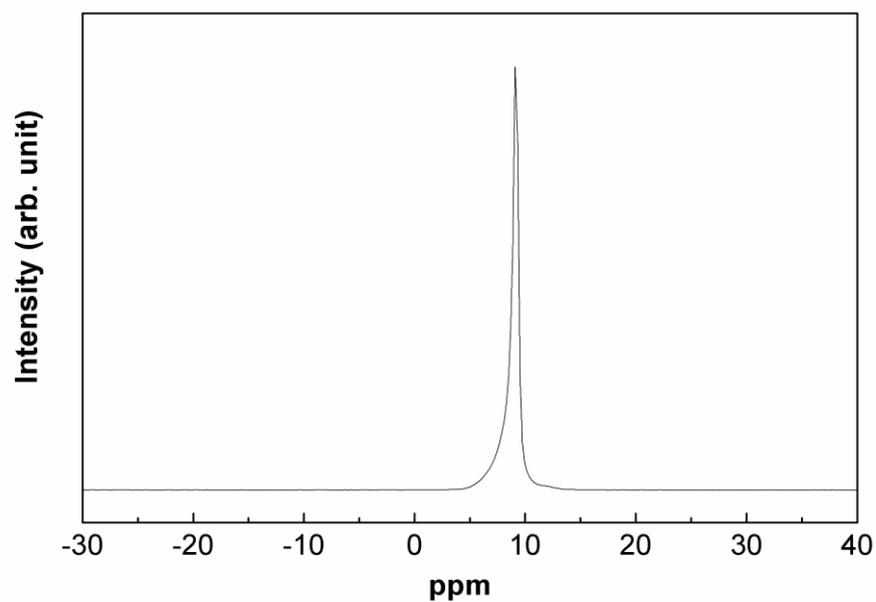


Fig. S2  $^{19}\text{F}$ -NMR spectrum of the anion in the bicontinuous cubic liquid-crystalline phase (339 K).

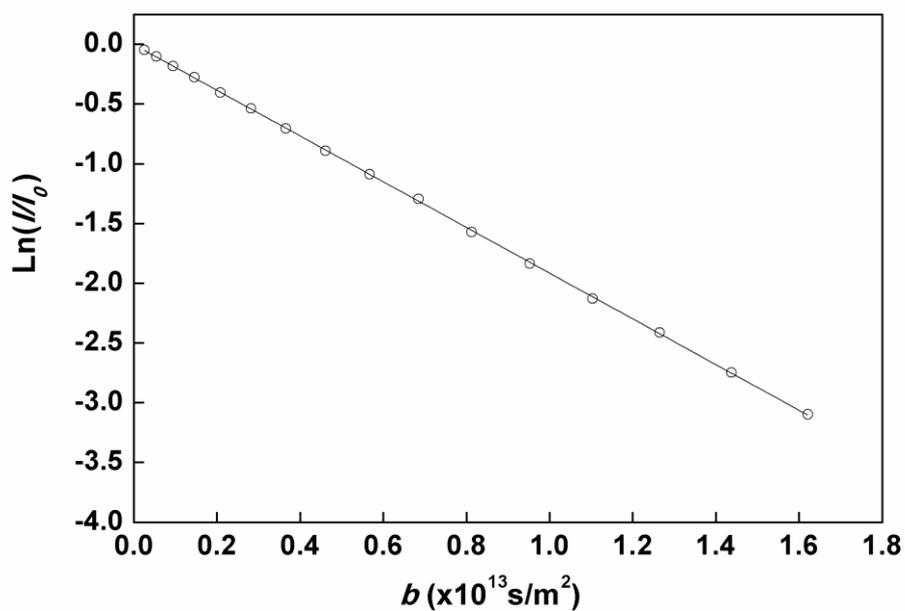
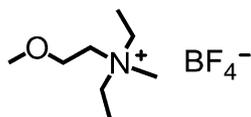


Fig. S3 Normalized signal amplitudes of a stimulated echo decay vs. the Stejskal-Tanner factor,  $b = (\gamma g \delta)^2 (\Delta - \delta/3)$ , for the anion in the bicontinuous cubic liquid-crystalline phase (339 K). The solid line is a linear fit with an adjusted  $R^2$ -value higher than 0.9999.



**Fig. S4** The molecular structure of diethyl-methyl-(2-methoxyethyl) ammonium tetrafluoroborate.

**Existence of poly-domains and its influence on diffusion.** In PFG-NMR spectroscopy large amounts of material are usually needed. Considering these large amounts it can be expected that liquid-crystalline samples are poly-domain. Consequently, the formation of diffusion barriers between domains is possible, which could result in artefacts in the diffusion measurements.

To evaluate the probability of such artefacts we consider the mean distance that a molecule can diffuse in our experiment. The mean square displacement (see below) is calculated from the diffusion coefficient ( $D$ ) and the diffusion time ( $\Delta$ , time delay between gradient pulses).

$$\begin{aligned}\langle x^2 \rangle &= 2 \times D \times \Delta \\ &= 2 \times 5 \times 10^{-13} \times 0.5 \\ &= 50 \times 10^{-14} \text{ [m}^2\text{]}\end{aligned}$$

The mean diffusion distance is the square root of this value.

$$\sqrt{\langle x^2 \rangle} \approx 7 \times 10^{-7} \text{ [m]}$$

From this we conclude that domain sizes on the  $\mu\text{m}$  scale can have an influence on the diffusion. Considering the slow cooling of the sample to liquid-crystalline phase we believe that the length scale of the domains should be larger than this value and domain barriers should therefore have a minimal effect on our measurements.

## References

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