Electronic Supplementary Material (ESI) for RSC Advances.
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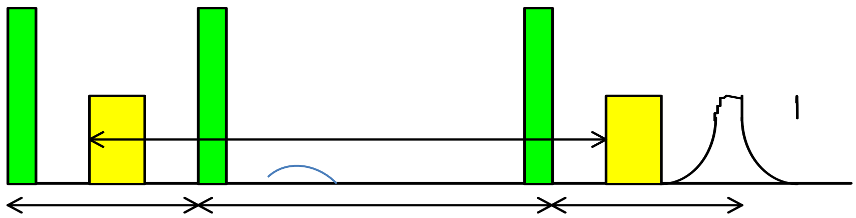
Supplementary material

I. PFG determinations (long range motions)

Self-diffusion coefficients can be determined with the PFG (pulse field gradient) technique. In these experiments, the stimulated echo $\pi/2$-t_1-$\pi/2$-t_2-$\pi/2$ sequence was used, in which two field gradient pulses of δ width and g intensity are applied between the two first $\pi/2$ and after the last $\pi/2$ radiofrequency pulse. In between second and third $\pi/2$ radiofrequency pulses a gradient spoiler is included (Fig. S1).



- gradient pulses: δ = 2 ms
- separation between gradient pulses: Δ= 10-100 ms
- field gradient: g (100-2500 G/cm)
- diffusion coefficient: D (m^2/s)

Figure S1. (a) Stimulated echo experiments used in determination of diffusion coefficients.

In PFG experiments, the echo attenuation can be described with the expression

$$A(2t_1+t_2)/A_0(2t_1+t_2)= \exp[-\gamma^2 \cdot g^2 \cdot \delta^2 \cdot (\Delta - \delta/3) \cdot D_{PFG}] = \exp(-b \cdot D_{PFG})$$

where A and A_0 stand for echo signal intensity at $(2t_1+t_2)$ with and without field gradient, γ is the nuclear gyro-magnetic ratio, and Δ is the diffusion time [23-25].

From the A/A_0 attenuation of the echo signal with $b = \gamma^2 \cdot g^2 \cdot \delta^2 \cdot (\Delta - \delta/3)$, diffusion D_{PFG} coefficients are deduced along the field gradient direction (z axis). From D_{PFG} values, MSD (mean square distances) can be deduced.

II. Restricted motions

Table S1: Mean square displacements and RMSD, calculated from D_{PFG} values measured at Δ=20 ms , are given as a function of temperature for the fast diffusing species in LTAP02-C sample.

T (K)	D_{PFG}	Δ	MSD=6. D_{PFG} .Δ	RMSD
294	$3.1x10^{-12}$	$2x10^{-2}$	$0.37x10^{-12}$	$0.61x10^{-6}$
312	$4.9x10^{-12}$	$2x10^{-2}$	$0.59x10^{-12}$	$0.77x10^{-6}$
332	$7.6x10^{-12}$	$2x10^{-2}$	$0.91x10^{-12}$	$0.95x10^{-6}$
352	$1.2x10^{-12}$	$2x10^{-2}$	$1.39x10^{-12}$	$1.18x10^{-6}$
373	$1.9x10^{-12}$	$2x10^{-2}$	$2.24x10^{-12}$	$1.50x10^{-6}$
392	$2.0x10^{-12}$	$2x10^{-2}$	$2.34x10^{-12}$	$1.53x10^{-6}$
412	$2.6x10^{-12}$	$2x10^{-2}$	$3.10x10^{-12}$	$1.76x10^{-6}$
432	$3.0x10^{-12}$	$2x10^{-2}$	$3.60x10^{-12}$	$1.90x10^{-6}$

Table S2: Mean square displacements and RMSD, calculated from D_{PFG} values measured at Δ = 20, 40 and 80 ms for increasing temperatures, are given for the LTAP04-C sample.

T (K)	D_{PFG} (m^2/s)	Δ (s)	MSD=6. D_{PFG} . Δ (m^2)	RMSD (m)
300	$8.66x10^{-12}$	$2x10^{-2}$	$1.04x10^{-12}$	$1.02x10^{-6}$
330	$1.26x10^{-11}$	$2x10^{-2}$	$1.51x10^{-12}$	$1.23x10^{-6}$
360	$1.72x10^{-11}$	$2x10^{-2}$	$2.07x10^{-12}$	$1.44x10^{-6}$
390	$2.40x10^{-11}$	$2x10^{-2}$	$2.87x10^{-12}$	$1.70x10^{-6}$
420	$2.79x10^{-11}$	$2x10^{-2}$	$3.34x10^{-12}$	$1.83x10^{-6}$
300	$5.27x10^{-12}$	$4x10^{-2}$	$1.26x10^{-12}$	$1.12x10^{-6}$
330	$7.85x10^{-12}$	$4x10^{-2}$	$1.88x10^{-12}$	$1.37x10^{-6}$
360	$1.22x10^{-11}$	$4x10^{-2}$	$2.93x10^{-12}$	$1.71x10^{-6}$
390	$1.62x10^{-11}$	$4x10^{-2}$	$3.89x10^{-12}$	$1.97x10^{-6}$
420	$1.85x10^{-12}$	$4x10^{-2}$	$4.45x10^{-12}$	$2.11x10^{-6}$
300	$3.61x10^{-12}$	$8x10^{-2}$	$1.73x10^{-12}$	$1.32x10^{-6}$
330	$5.58x10^{-12}$	$8x10^{-2}$	$2.68x10^{-12}$	$1.64x10^{-6}$
360	$7.82x10^{-12}$	$8x10^{-2}$	$3.76x10^{-12}$	$1.94x10^{-6}$
390	$1.08x10^{-11}$	$8x10^{-2}$	$5.16x10^{-12}$	$2.27x10^{-6}$
420	$1.28x10^{-12}$	$8x10^{-2}$	$6.15x10^{-12}$	$2.48x10^{-6}$

Table S3: Mean square displacements and RMSD, calculated from D_{PFG} values measured at Δ=20 ms for the two sol-gel samples.

Sample	T (K)	D_{PFG} (m^2/s)	Δ (s)	MSD=6·D_{PFG}·Δ(m^2)	RMSD (m)	q_m^{-1}
LTAP03-SG	294	$2.8x10^{-12}$	2.10^{-2}	$0.34x10^{-12}$	$0.58\ x10^{-6}$	$1.25x10^{-6}$
LTAP04-SG	**294**	$2.3x10^{-12}$	2.10^{-2}	$0.27x10^{-12}$	$0.53\ x10^{-6}$	$1.21x10^{-6}$

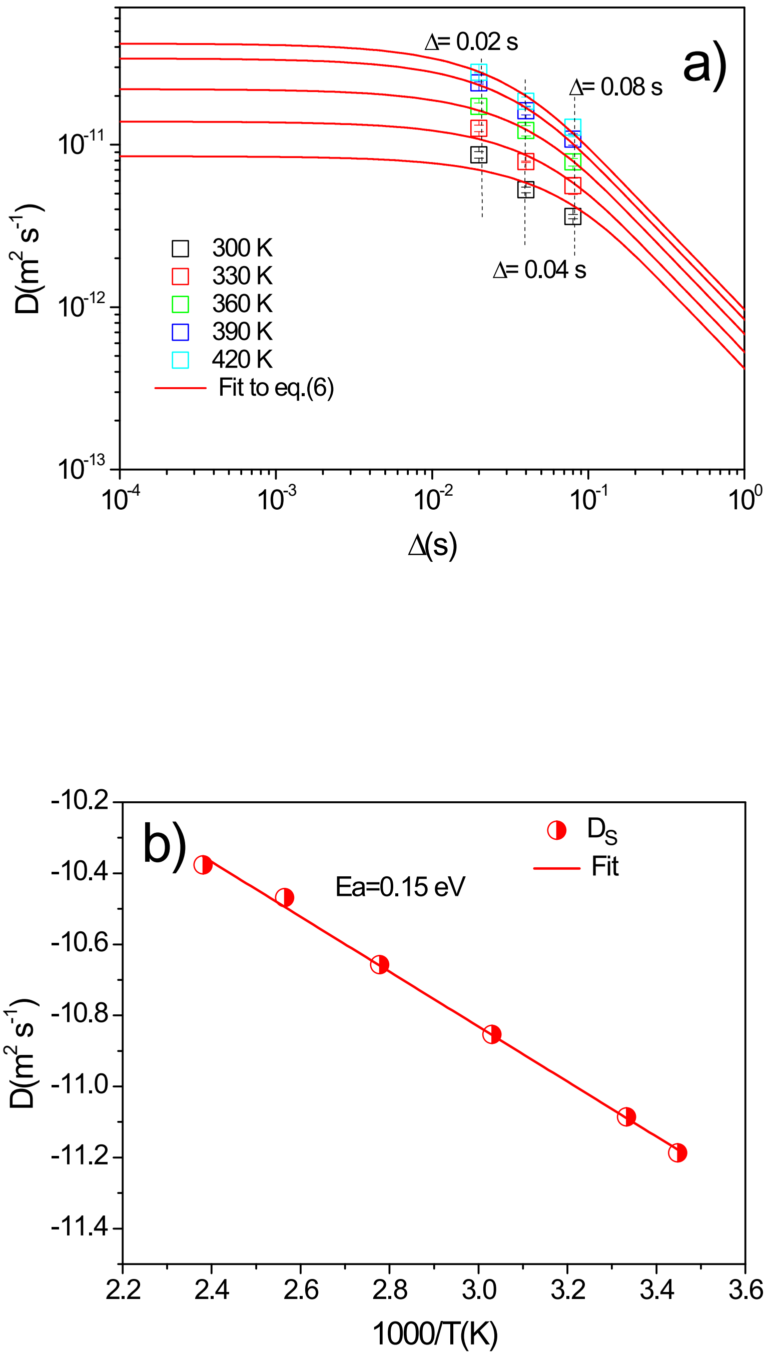


Figure S2: a) Dependence of experimental D_{PFG} (Δ,T) values (LTAP04-C sample), on increasing temperatures. The lines are the fits to experimental D_{PFG} (Δ) using the eq (6) at each temperature. b) Ahrrenius Fit of the deduced Ds(T) values.

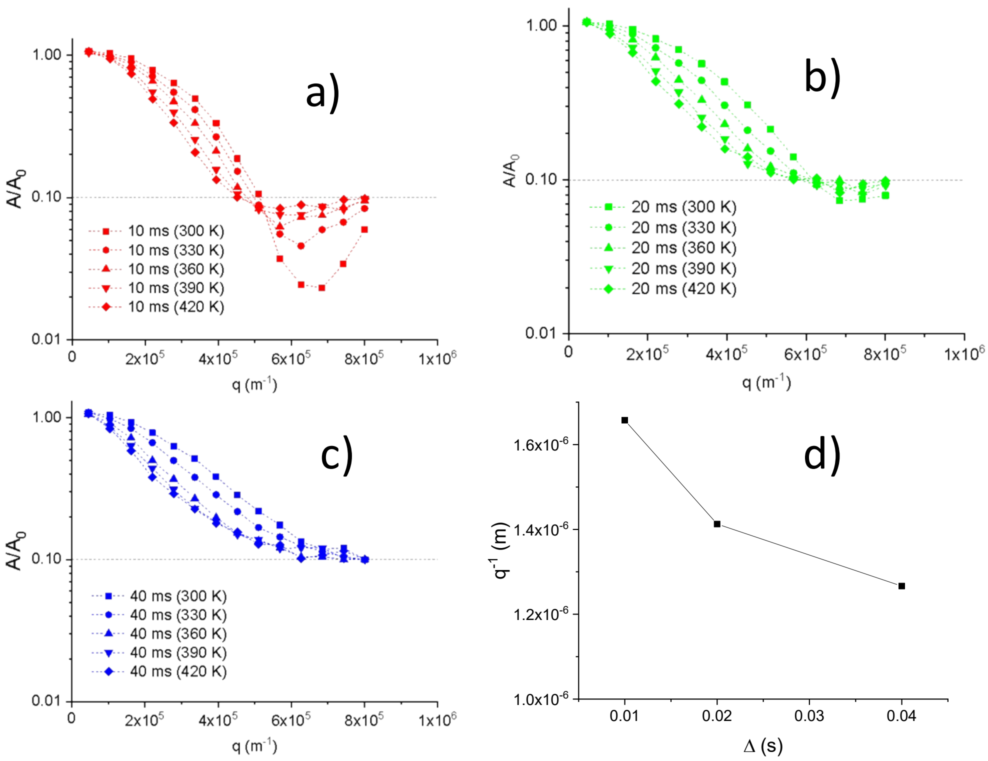


Figure S3. Echo attenuation in q-space (m^{-1}) for different temperatures at three diffusion times (Δ) a): 10, b): 20 and c): 40 ms in LTAP04-C. (δ = 2.0 ms). d) The diffraction distances (q^{-1}) vs Δ values.

III. NMR Relaxometry

The analysis of 1/T1 and 1/T2 values as a function of the temperature, showed the presence of two relaxation mechanisms in the LTAP02-C sample (Fig. S2) . The 7Li NMR

spin-lattice relaxation times (T_1) were measured with a SXP 4/100 Bruker spectrometer. Determination of T_1 values at each temperature was done by using the classical π-τ - π/2 sequence. The frequencies used were 31, 20, and 10.6 MHz and the experiments were carried out between 100 and 500 K. Determination of T_2 values at each temperature was done .... Analysis of spectra was carried out with the Winfit program (Bruker). This program allows the position, line width, and intensity of the components to be determined by using a nonlinear iterative least-squares method.

Experimental $1/T_1$ and $1/T_2$ results were fitted with expressions

$$T_2^{-1} = \frac{1}{2}C'\left[3\tau + \frac{5\tau}{1+(\omega_0\tau)^{1+\beta}} + \frac{2\tau}{1+(2\omega_0\tau)^{1+\beta}}\right]$$

$$T_1^{-1} = C\left[\frac{\tau}{1+(\omega_0\tau)^{1+\beta}} + \frac{4\tau}{1+(2\omega_0\tau)^{1+\beta}}\right]$$

where C and C', describe magnetic interactions that produce spin-lattice and spin-spin relaxations, ω_0 is the NMR frequency, β is the Li motion correlation parameter and τ is the correlation (residence) time described with the expression

$$\tau = \tau_0^R \exp(E_M^R/kT)$$

where T is the temperature, τ_0^R is the correlation time at infinite temperature and E_M^R is activation energy for Li motions.

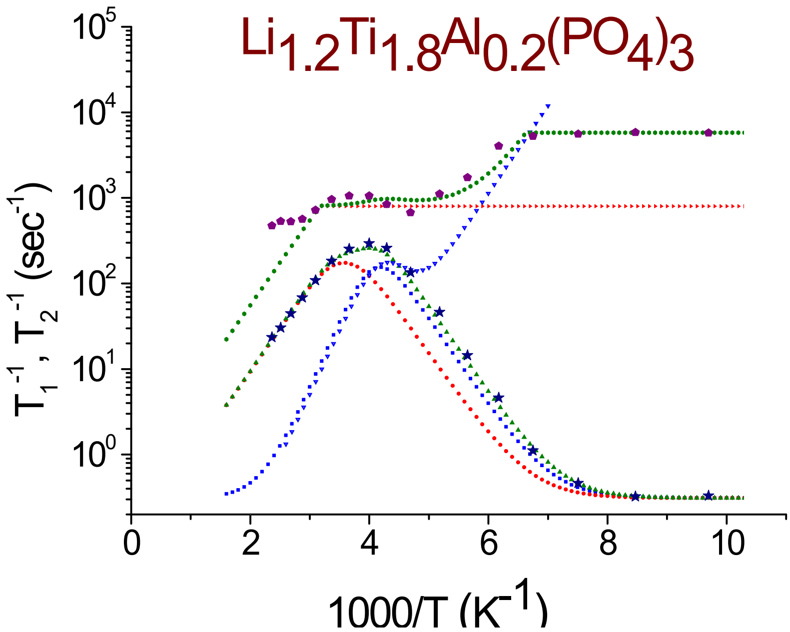


Figure S4: *Dependence of $1/T_1$ and $1/T_2$ values on the inverse temperature. The fitting of experimental data was performed with two relaxation mechanisms.*

The local hopping from M1 to M12 and from M12 to M3 sites is responsible for two relaxation mechanisms detected at increasing temperatures in $1/T_1$ and $1/T_2$ plots (Fig. S4). At two $1/T_1$ maxima, residence times are ~ $1/\omega_0$ ~ 10^{-8} s. At the LT regime, local motions are produced, however at the HT regime, extended motions along …M3-M1-M3… are dominant. Taken into account that hopping distance is ~ 6 Å between M3 sites, a diffusion coefficient D_S ~ $5x10^{-12}$ m^2/s was deduced at 300K, for the HT regime in the LTAP02 sample (see manuscript).