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Highly Mobile Ions: Low-Temperature NMR Directly Probes Extremely Fast Li^+ Hopping in Argyrodite-Type Li_6PS_5Br

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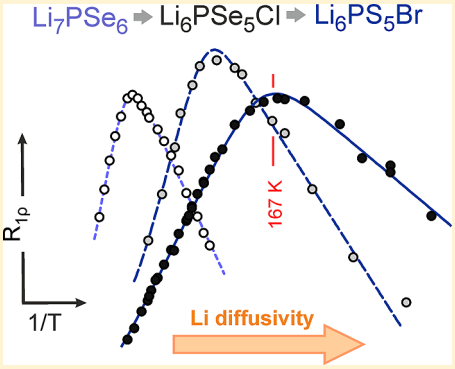
Supporting Information

ABSTRACT: The development of safe and long-lasting all-solid-state lithium-ion batteries needs electrolytes with exceptionally good transport properties. Here, we report on the combination of several solid-state nuclear magnetic resonance (NMR) techniques which have been used to precisely probe short-range as well as long-range Li^+ dynamics in Li_6PS_5Br from an atomic-scale point of view. NMR data clearly reveal an extraordinary high Li diffusivity. This manifests in so-called diffusion-induced spin−lattice relaxation NMR rate peaks showing up at temperatures as low as 260 K. From a quantitative point of view, at ambient temperature the Li jump rate is of the order of 10^9 s^{-1} which corresponds to a Li^+ conductivity in order of 10^{-3} to 10^{-2} S/cm, thus, indicating "liquid-like" Li^+ diffusion behavior in Li_6PS_5Br.



SECTION: Kinetics and Dynamics

Since the discovery of ionic conduction in solids many decades ago, the research field, which is frequently known as *solid state ionics* today, has emerged to be one of the most important subdisciplines of physical chemistry, in particular, and materials science, in general. Currently, this ongoing progress is additionally driven by the increasing demand to realize advanced and energy-dense electrochemical storage systems that need fast ion conductors.

Looking toward improved lithium-ion batteries[1−4] for, for example, electric vehicles as well as for storing energy from renewable but intermittent sources, new materials with extraordinary transport properties have to be developed, thoroughly characterized, and tested. To go beyond today's commercially available systems, which mostly rely on flammable liquid electrolytes, more than ever before, *solid* electrolytes[5] are indispensable to guarantee both safety and reliability as well as a long life of a rechargeable battery.

Besides thermal and electrochemical stability, a powerful solid electrolyte, which conducts lithium ions between the negatively charged anode and the positive cathode, needs to have an Li ion conductivity higher than 10^{-3} S/cm near room temperature. So far, only a few crystalline solids are known[5−12] that meet these requirements. Once promising candidates are found, Li transport parameters have to be precisely and reliably measured.[13] However, in the case of lithium the pool of methods is rather limited. For example, because there is no suitable long-living isotope known, the well-known radio tracer method cannot be applied. Conductivity spectroscopy needs careful postpreparation of the sample and might suffer from porosity, grain boundary resistances, and electrode effects.[14] Nuclear magnetic resonance (NMR) spectroscopy,[15−20] however, which takes advantage of the superb receptivity of the ^{7}Li nucleus (spin-3/2), represents an atomic-scale, nondestructive, and even contactless method to be used for this purpose. Moreover, the combination of complementary time-domain NMR techniques allows probing Li diffusion parameters over a large dynamic range, covering in the best case more than 10 decades.[19,21,22]

We report on an example par excellence where relaxation NMR was used to directly probe Li jump rates $1/\tau$ and activation energies E_a in argyrodite-type cubic Li_6PCh_5X (Ch = S, Se; X = Cl, Br),[14,23,24] representing a new class of highly conducting solid electrolytes. It turned out that polycrystalline Li_6PS_5Br belongs, as yet, to one of the fastest solid Li conductors investigated by Li NMR. The results even exceed those recently reported for an ultrafast jump diffusion process in $Li_{12}Si_7$.[25] Finally, by systematically comparing the results of different members of the Li_6PS_5Br family, the measurements helped us to understand how anion substitution may improve cation diffusivity − a general concept that is extremely advantageous to tailor transport properties. Let us note that, even today, a knowledge-based and target-oriented development of functional materials, in the true sense of the word, has been documented extremely rarely.

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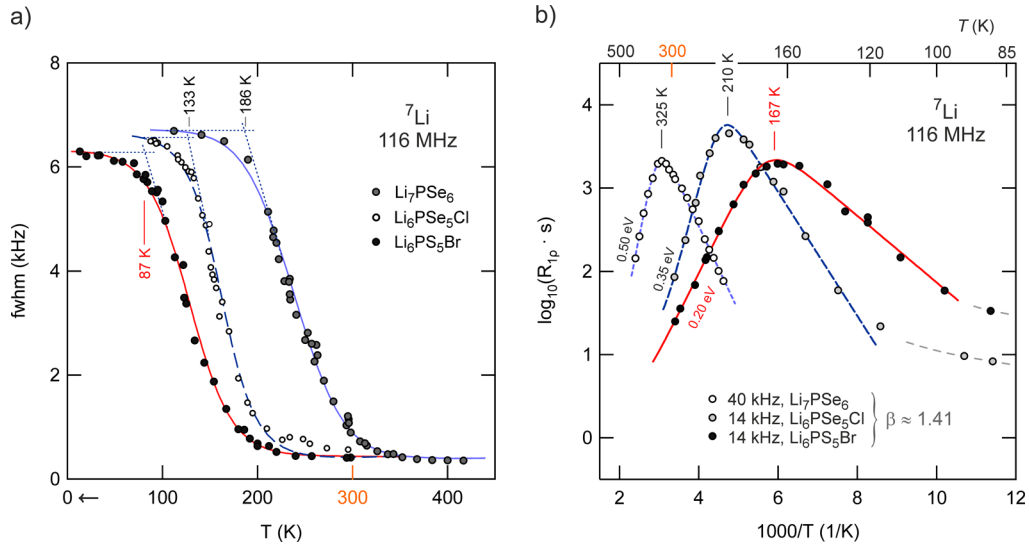

Figure 1. (a) Temperature dependence of the ^{7}Li NMR line widths (full width at half-maximum) of three selected Li-argyrodites. Data for Li_7PSe_6 were taken from ref 32. Lines are to guide the eye. Dotted lines indicate the determination of the onset of motion-induced line narrowing. A value of 87 K, which is obtained for Li_6PS_5Br, indicates extremely fast hopping processes. (b) Arrhenius plot of the corresponding ^{7}Li SLRρ NMR rates recorded at the locking frequencies indicated. Here, at the peak maximum, the Li jump rate is at least 10^5 s $^{-1}$. The lines represent fits according to a modified BPP relaxation model,[13,36,37] taking into account its asymmetry by introducing the parameter β. The farther the diffusion-induced NMR relaxation peak is shifted toward lower T, the faster Li exchange and the smaller the activation energy turns out. The latter is directly given by the slope of the respective high-temperature flank. In summary, Li diffusion drastically increases in the following order: Li_7PSe_6 < Li_6PSe_5Cl < Li_6PS_5Br. See the text for further details.

The Li-argyrodites, with natural Li abundance (^{7}Li 92.5%, ^{6}Li 7.2%), were prepared by solid-state synthesis; details of sample preparation are described elsewhere.[14] To protect the polycrystalline powder samples permanently from any traces of moisture they were carefully fire-sealed in glass ampules. ^{7}Li NMR line shapes and spin−lattice relaxation (SLR) measurements in both the laboratory and rotating frame of reference were recorded on a digital Avance III NMR spectrometer that is connected to a shimmed cryo magnet with a nominal magnetic field of 7 T. (See the Supporting Information for further experimental details.) Because of the high diffusivity of the Li ions in Li_6PS_5Br the NMR measurements had to be partly performed at cryogenic temperatures as low as 13 K. For that purpose a special probe designed by Bruker was employed. While line shapes were recorded with a single pulse, SLR NMR rates were acquired using the saturation recovery technique[17,26] and a spin-lock pulse sequence,[26−28] respectively.

First insights into Li dynamics of crystalline solids can be deduced from the motion-induced narrowing of static Li NMR spectra recorded at different temperatures.[29,30] At sufficiently low T, that is, in the so-called rigid-lattice regime, the Li jump rate $1/\tau$ is much smaller than the spectral width of the usually dipolarly broadenend Gaussian NMR central line. With increasing temperature, however, Li exchange processes become faster, and $1/\tau$ reaches values being comparable to the spectral width. The associated averaging of dipole−dipole interactions results in a motionally narrowed, in many cases, Lorentzian NMR central line.[31] This behavior is also observed in the present case. For comparison, in Figure 1a, the NMR line widths (full width at half-maximum) for three selected Li-argyrodites are plotted versus temperature. While onset of motional narrowing (MN) for Li_7PSe_6 significantly starts at T_{MN} = 186 K,[32] the corresponding curve of Li_6PSe_5Cl is clearly shifted toward lower temperature yielding T_{MN} = 133 K. This value is comparable to that found recently for the ultrafast diffusion process in polycrystalline $Li_{12}Si_7$. At the onset point of the narrowing curve the jump rate $1/\tau$ is expected to be on the order of 10^3 s^{-1}. Most importantly, a further shift is observed for Li_6PS_5Br, resulting in an extremely low onset temperature of T_{MN} = 87 K (Figure 1a). The results nicely corroborate those reported by Eckert and coworkers,[7] who recorded NMR spectra down to 130 K, as well as confirm the data presented by Koch.[33] To verify such ultrafast diffusion processes, we measured diffusion-induced ^{6}Li and ^{7}Li SLR NMR rates at different frequencies and over a broad temperature range.

Provided SLR is solely induced by diffusion processes, the NMR SLR rate $R_{1(\rho)}$ passes through a maximum on a $\log(R_{1(\rho)})$ versus $1/T$ plot.[13,17,34] When $R_{1(\rho)}$ reaches its maximum value the mean correlation rate, being almost identical to the Li jump rate $1/\tau$, was on the order of the Larmor (ω_0) or locking frequency (ω_1) used to sample the NMR rates.[13,17] Because ω_0 is in the megahertz range and ω_1 is on the order of kilohertz, complementary SLR NMR experiments are sensitive to motional processes covering a quite large time scale. Let us first discuss those carried out at comparable locking frequencies of $\omega_1/2\pi$ = 45 and 14 kHz, respectively (see Figure 1b).[35] While Li_7PSe_6 reveals an asymmetric rate peak showing up at T_{max} = 325 K, that of the Cl-containing argyrodite shows up at 210 K, indicating greatly improved Li diffusion; in the case of *rotating frame* SLRρ, at T_{max}, the jump rate is given by $1/\tau$ $(T_{max}) \approx 2\omega_1$,[13,17] thus, being on the order of 10^6 s^{-1}. In perfect agreement with the line width measurements (Figure 1a), the rate peak $R_{1\rho}(1/T)$ of Li_6PS_5Br, which was recorded at $\omega_1/2\pi$ = 14 kHz, is shifted toward even lower T yielding T_{max} = 167 K (Figure 2b). For comparison, considering other fast ion conductors studied, a value on the order of 10^5 jumps per second is usually found slightly below room temperature.[21] Here the shift of more than 100 K toward lower T unequivocally classifies Li_6PS_5Br as an electrolyte with fast Li exchange processes.

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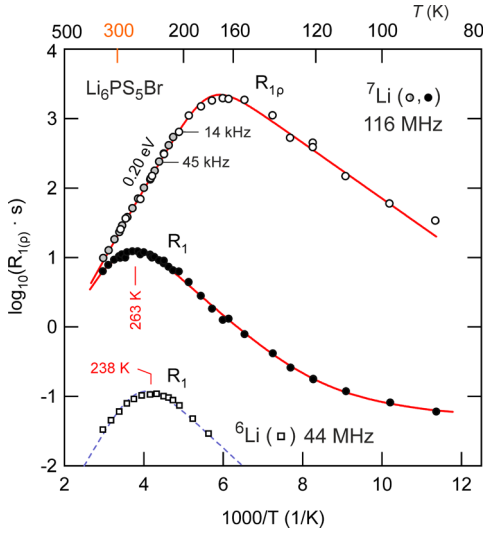

Figure 2. Arrhenius plot of the ^{7}Li NMR relaxation rates R_1 and $R_{1\rho}$ of polycrystalline Li_6PS_5Br measured in both the rotating frame (see Figure 1b) and laboratory frame of reference. Solid lines represent a joint fit being based on the BPP model (see text). For comparison, the diffusion-induced ^{6}Li SLR NMR rates recorded at 44 MHz are also included. Li SLR NMR rate maxima, showing up at 263 and 238 K, that is, well below room temperature, point to extremely fast, translational Li ion motions with jump rates of the order of 10^9 s^{-1}, that is, residence times as low as 1 ns.

At room temperature, the jump rate of Li_6PS_5Br is expected to reach even larger values. Indeed, SLR NMR measurements performed at a resonance frequency of 116 MHz reveal a diffusion-induced rate peak $R_1(1/T)$ passing through its maximum at T_{max} = 263 K (Figure 2). This has been corroborated by complementary ^{6}Li measurements carried out at 44 MHz yielding T_{max} = 238 K (see also Figure 2). With $1/\tau(T_{max}) \approx \omega_1$, being valid for SLR NMR in the *laboratory frame* of reference,[17] this yields $1/\tau$ (238 K) = 2.8 × 10^8 s^{-1} and $1/\tau$ (263 K) = 7.3 × 10^8 s^{-1} ≈ 10^9 s^{-1}, respectively. Thus, well below room temperature the mean residence time of a Li ion is close to 1 ns. To our knowledge this is so far one of the fastest solid-state diffusion processes probed by time-domain ^{6,7}Li NMR relaxometry. For comparison, in $Li_{12}Si_7$, the $R_1(1/T)$ rate peak shows up at much higher temperatures (viz. T_{max} = 400 K) when measured at 77.7 MHz.[25]

The jump rates derived from SLR NMR can be converted into conductivity values according to the Einstein−Smoluchowski equation and the Nernst−Einstein equation.[38] The first interrelates $1/\tau$ with the self-diffusion coefficient: assuming 3D diffusion and a jump distance of 2.5 Å, which is a very reasonable value in the present case,[39] we obtain $D_{263K} = a^2/(6\tau)$ = 7.6 × 10^{-8} cm^2 s^{-1} (in a relatively theory-independent way). Disregarding any correlation effects, by means of the Nernst−Einstein equation, D_{263K} can roughly be converted into a conductivity value σ. Here a mean residence time of 1 ns corresponds to σ in the order of $\sigma \approx 10^{-2}$ S/cm, clearly illustrating extremely mobile lithium ions in polycrystalline Li_7PS_5Br (see below). Certainly, this conversion should be regarded as a rough estimate because relaxation NMR and conductivity spectroscopy sense different kinds of correlation functions.[40,41]

To understand the motion-induced ^{7}Li SLR NMR rates of Li_7PSe_6, Li_6PSe_5Cl, and Li_6PS_5Br in more detail, we used modified BPP-type[42] spectral density functions $J(\omega_0,\tau_c)$ and $J(\omega_0, \omega_1, \tau_c)$ that are based on exponential motional correlation functions[17,42] $G(t')$ to describe the temperature dependence of $R_1(1/T)$ and $R_{1\rho}(1/T)$, respectively.[13,25,34] The correlation time τ_c is within a factor of 2[17] identical to the Li residence time $\tau = \tau_0 \exp(-E_a/(k_BT))$; here E_a denotes the activation energy and k_B is Boltzmann's constant.

The Lorentzian-shaped function J, which is directly proportional to R_1 and $R_{1\rho}$, can be derived from G by Fourier transformation.[17,43] In the case of a 3D diffusion process, we have $J \propto \tau$ at high temperatures, that is, in the limit $\omega_{0(\rho)}\tau \ll 1$, and $J \propto \tau^{-1}\omega_{0(\rho)}^{-\beta}$ (with $1 < \beta \leq 2$) in the low T limit where $\omega_{0(\rho)}\tau \gg 1$ holds.[17,34] Original BPP-type behavior[36] does not take into account correlation effects and predicts $\beta = 2$ leading to symmetric relaxation rate peaks.[17,44] Asymmetric peaks are usually found for structurally complex or even disordered ion conductors.[6,13,34] Such materials reveal a broad range of short-range and long-range motional processes that are affected by correlation effects[45] resulting from, for example, Coulomb interactions.[46] In the present case, the $R_{1\rho}(1/T)$ fits yield an asymmetry parameter $\beta_\rho \approx 1.4$ (Figure 1b), while $\beta \approx 1.5$ is found for the ^{7}Li NMR (and ^{6}Li NMR) rates recorded in the laboratory frame of reference (see Figure 2). The small difference in β points to slightly differing correlation effects affecting the SLR NMR rates, which are per se sensitive to Li motions on different time scales.[34]

It is clearly evident from Figure 1b that E_a, which can be independently deduced from the slope of the high-T flank, decreases from ∼0.5 eV in steps of 0.15 eV. This result is in excellent agreement with the shift of the rate peaks observed: the smaller E_a, the faster Li diffusion becomes. Thus, Li exchange drastically increases in the following order: Li_7PSe_6 (≈ Li_7PS_6) < Li_6PSe_5Cl < Li_6PS_5Br. Let us note that Li_7PSe_6, investigated in ref 32 in detail, is expected to show very similar diffusion parameters as the S-analogue Li_7PS_6. The value found for Li_6PSe_5Cl (0.35 eV) is in good agreement with the one calculated by Rao et al. characterizing the 3D long-range pathway network.[23]

The lowest value, E_a = 0.20(1) eV (200 K < T < 330 K, see Figure 2), is also found when the NMR peaks $R_{1\rho}(1/T)$ and $R_1(1/T)$ of Li_6PS_5Br are analyzed in terms of a global fit (solid lines in Figure 2), that is, linking the fitting parameters such as ω_0, the activation energies, and coupling constants. In the present case, however, the best fit is obtained when $\beta \neq \beta_\rho$ (see above) and $1/\tau_0$ of SLR NMR is independent of that used to parametrize the $R_{1\rho}(1/T)$ peak. It is worth noting that nondiffusive background relaxation, see the SLR NMR rates of Figure 2, which were recorded below 120 K, were taken into account by an appropriate power law: $R_1 \propto T^\kappa$ with $\kappa \approx 2$. Such effects, which are also seen in Figure 1b, presumably represent SLR induced by lattice vibrations or by coupling of the Li spins with traces of paramagnetic impurities. Moreover, from many different runs of the global fit procedure it turned out that it is useful to replace ω_1 = 14 kHz × 2π with a slightly larger value of ω_{eff} = 1.4 ω_1. Here the factor of 1.4 takes into account local magnetic fields in the order of the locking field.

For comparison, the fitting results obtained are listed in Table 1. Interestingly, the $R_{1\rho}$ data seem to underestimate the Arrhenius prefactor, leading to τ_0 = 6(2) × 10^{-12} s, while the $R_1(1/T)$ peak yields τ_0 = 2(1) × 10^{-13} s. The latter value, whose inverse agrees with the typical range of phonon frequencies, is corroborated by analyzing the ^{6}Li $R_1(1/T)$ rate peak, which is best characterized by τ_0 = 3(1) × 10^{-13} s.

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Table 1. Results (E_a,[b] $\beta_{(\rho)}$, τ_0, and the pre-factor C[c]) of the overall SLR NMR Fit Shown in Figure 2 (solid lines)[a]

	E_a[b]	C[c]	$\beta_{(\rho)}$	τ_0
R_1 (^{7}Li)	0.20(1) eV	5.8(1) × 10^9 s^{-2}	1.54	2(1) × 10^{-13} s
$R_{1\rho}$ (^{7}Li)			1.36	6(1) × 10^{-12} s
R_1 (^{6}Li)	0.20(3) eV	2(1) × 10^7 s^{-2}	1.53	3(1) × 10^{-13} s

[a]The fit was carried out using $\omega_{1,eff} = 1.4\ \omega_1$ with $\omega_1 = 14$ kHz × 2π, $\omega_0(^7\text{Li}) = 116$ MHz × 2π, and $\omega_0(^6\text{Li}) = 44$ MHz × 2π. [b]This value refers to the slope of the high-T flank of the SLR NMR peaks. [c]The prefactor C interrelates $J(\omega_0,\tau_c)$ with the relaxation rate R_1. Values ranging from 10^9 to 10^{10} s^{-2} correspond to the square of typical ^{7}Li quadrupole coupling constants.[31] Note that the quadrupole moment of ^{6}Li is by a factor of 50 smaller than that of ^{7}Li; therefore, for ^{6}Li NMR, the dipolar contributions play a non-negligible role.

Thus, describing (long-range) Li diffusion in Li_6PS_5Br with a single Arrhenius relation, the jump rate $\tau(T)$ is given by $\tau = 3(1) \times 10^{-13}$ s·exp(− 0.20(2) eV/(k_BT)). According to that result, at $T = 125$ K, that is, at the temperature of the inflection point of the NMR motional narrowing curve of Li_6PS_5Br (see Figure 1b), the jump rate $1/\tau$ should be on the order of 3.5 × 10^4 s^{-1}. Indeed, with the rigid lattice line width $\Delta\nu_{rl} = 6$ kHz, the estimation $1/\tau \approx \Delta\nu_{rl} \times 2\pi$ yields 3.9 × 10^4 s^{-1}. Certainly, this agreement does not rule out the presence of other, quite different and temperature-dependent diffusion processes. In particular, while activation energies determined in the limit $\omega_{0(\rho)}\tau \ll 1$ are generally compared with those from dc-conductivity probing long-range ion transport,[17,34] the low-T flank of the $R_{1\rho}(1/T)$ rate peak is influenced by short-range motional processes characterized by much smaller activation energies;[34] here, this is 0.08(2) eV for Li_6PS_5Br and 0.15(2) eV for the Cl-analogue; cf. also results from theoretical studies including also I-containing compounds.[23,39]

Finally, it is highly useful to compare the absolute values of the purely diffusion-induced ^{6}Li (spin-1) NMR rates in the limit $\omega_0\tau \ll 1$ with those of the corresponding ^{7}Li (spin-3/2) NMR rate peak. For dipolar interactions being responsible for SLR NMR, the ratio $R_1(^6\text{Li})/R_1(^7\text{Li}) = r$ is expected to be on the order of two, while for quadrupolar relaxation r should be on the order of 10^{-4}.[47] Experimentally we found 5.3(2) × 10^{-3} pointing to a quadrupolar mechanism influencing ^{7}Li NMR spin−lattice relaxation here.

In conclusion, among the Li-argyrodites studied here, Li_6PS_5Br turned out to be a material with an exceptionally high Li diffusivity. The corresponding long-range jump process is characterized by a hopping activation energy of only 0.2 eV as deduced from the various temperature-variable NMR SLR measurements. This extraordinary feature manifests in (laboratory frame) SLR NMR rate peaks showing up at temperatures as low as 260 K. From a quantitative point of view, at room temperature, this yields a Li jump rate of 10^9 s^{-1}, which corresponds to an Li^+ conductivity on the order of 10^{-3} to 10^{-2} S/cm, thus indicating "liquid-like" diffusion behavior comparable to, for example, the interlayer process in Li_3N.[48] The activation energy and the estimated ionic conductivity from SLR NMR are in agreement with results deduced from previous and recent conductivity studies.[7,23,49] Let us note that in the limit of $\omega_{0(\rho)}\tau \ll 1$, SLR NMR is expected to yield activation energies being comparable to those characterizing long-range ion transport, while on the low-T side of a given NMR relaxation peak, localized, that is, short-range, Li motional processes are probed.[17,34]

The high Li diffusivity found makes the development of safe and long-lasting all-solid-state lithium batteries feasible. It might be understood by comparing the results from the three different samples studied: because Li diffusivity increases from Li_7PSe_6 to Li_6PSe_5Cl (and Li_6PS_5Br), the structural mismatch and strain generated by substitution of a large halogen ion for, for example, selenium, seems to be highly relevant when a high Li mobility needs to be achieved. Moreover, the larger Li diffusivity of Li_6PS_5Br against Li_6PSe_5Cl might be attributed to the combination of anions with different polarizabilities. In summary, the present example illustrates how anion substitution can be used as a tool to successfully manipulate cation diffusivity in a crystalline solid.

■ ASSOCIATED CONTENT

Supporting Information

Cf. for experimental details including information on the equipment used, the measurement conditions chosen, and the pulse sequences applied to record the SLR NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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