Supplementary Material (ESI) for Chemical Communications

Porous Inorganic Capsules in Action: Modelling Transmembrane Cation-Transport Parameter-Dependence Based on Water as Vehicle

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Concentration dependence:

Concentration dependencies of ^{7}Li NMR signals can be related to the concentration dependent extent of interaction with a counter-ion or dipole.[6] As expected for a quadrupole nucleus (spin 3/2, nuclear quadrupole moment –4.1 fm^2)[7] in an environment of non-cubic symmetry, the high-field resonance lines, corresponding to Li^+ connected to the capsule (cf. *C* in Fig. 1), are comparatively broad while six different Li^+ sites have tentatively been indicated by red lines in Fig. S1. The comparably sharp low-field signal reflects the solvated free lithium cations, $[Li(dmso)_n]^+$. The relative peak intensities remain constant which proves that the sites, corresponding to Fig. 1*B*, remain invariably populated by Li^+ independent of the concentration. The differences in the overall signal shapes reflect variations of the chemical shift δ with concentration.

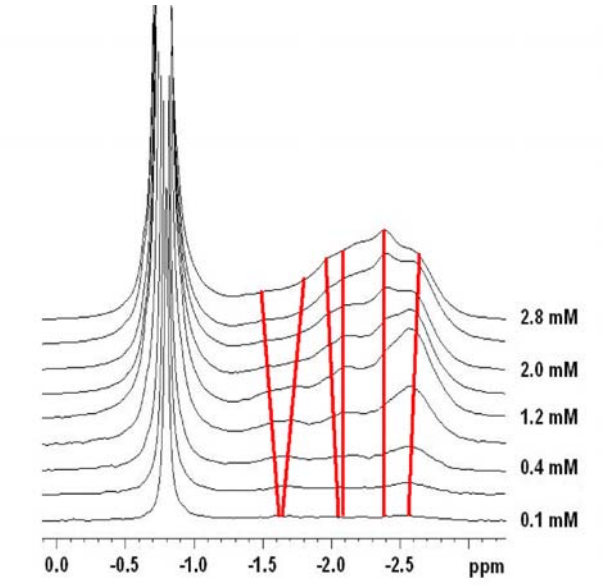

Fig. S1 Concentration dependence of the ^{7}Li NMR resonances of **1** in DMSO showing, along with $[Li(dmso)_n]^+$, different high-field resonances due to the different sites occupied by Li^+. The indicated concentrations correspond to *c*(**1**); for *c*(Li), *c*(**1**) should be multiplied by 28. The six red lines indicate six tentative Li^+ assignment sites associated with **1a**.

Influence of cryptands:

Addition of small amounts of the cryptand C211 (c(C211) = 0.1-0.5 mM) to a 0.8 mM solution of **1** in DMSO produces a new signal at -0.1 ppm, which grows at the expense of the $[Li(dmso)_n]^+$ signal as c(C211) is gradually increased, leaving the $\{Li^+ \subset \mathbf{1a}\}$ sites essentially unaffected. As c(C211) is further increased, $\{Li^+ \subset \mathbf{1a}\}$ sites are gradually depleted. An excess of C211 completely removes the upfield signals, and a single signal appears at δ = -0.2 ppm. The same effect is observed as excess C211 is added to solutions of **1** in DMF or NMP; the resulting singlets are at -0.40(3) ppm. The diameter of the cavity of C211 matches the diameter of the unsolvated lithium ion which leads to a very high complex stability (larger than that of $[Li^+(H_2O)_n]^+$); the chemical shift of -0.4 corresponds to that reported for $[Li(C211)]^+$.[8] In contrast, the crown ethers 15C5 and 12C4, which complex Li^+ less effectively than C211, do not influence the population of the $\{Li^+ \subset \mathbf{1a}\}$ sites.