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Selective lithium ion recognition in self-assembled columnar liquid crystals based on a lithium receptor†

Yuan Luo, Nicolas Marets and Takashi Kato*

Lithium is recognized as being significantly important due to its various applications in different areas especially in energy technology. In the present study, self-assembled nanostructured liquid-crystalline (LC) materials, that selectively bind lithium cations, have been developed for the first time. Wedge-shaped crown ether derivatives bearing dibenzo-14-crown-4 (DB14C4) or 12-crown-4 moieties are able to act as LC lithium-selective receptors. We have found that complexation of these receptors with lithium perchlorate induces liquid-crystalline columnar phases, while sodium perchlorate is immiscible with both receptors. Remarkably, a receptor consisting of DB14C4 as an effective lithium-selective ligand exhibits high selectivity for LiCl over NaCl, KCl, RbCl and CsCl. The lithium selectivity was demonstrated and investigated by ^{1}H NMR, ^{1}H COSY and FT-IR spectroscopic measurements. The preferred coordination number of four and the ideal cavity geometry of the DB14C4 moiety of the receptor are shown to be key factors for the high lithium selectivity. This new design of LC lithium-selective receptors opens unexplored paths for the development of methods to fabricate nanostructured materials for efficient selective lithium recognition.

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Introduction

Lithium has been attracting considerable attention due to its extensive applications in modern battery technology, glass and ceramics processing, lubricants and pharmaceuticals.[1–4] The majority of lithium currently produced comes from salt-lake brines by solar evaporation processes.[5] As the demand for lithium has begun to grow dramatically after the turn of the century, mining lithium in a more efficient and economically-feasible way is of great interest.[6,7] Many efforts have been devoted to developing new methodologies/techniques for extracting lithium.[8–13] However, lithium cations are still difficult targets for selective recognition and purification because of their large hydration energy and the coexistence of other similar alkali metal cations.[14,15] The design of new functional receptor systems may contribute to the development of efficient selective lithium recognition.

Nature has been a source of inspiration for the development of artificial functional systems.[16–21] The extraordinary selective and efficient transport of specific ions across the cell membrane is common and essential to many of life's processes.[22,23] This ion-transport ability is owed to ionic channels with characteristic architectures and coordination geometries created by membrane proteins.[23–28] Inspired by these discoveries in biological systems, artificial ionic channels that are capable of transporting protons or alkaline metal ions efficiently have been developed.[18,29–36] But lithium cation selective ionic channels have not yet been achieved.

Liquid-crystalline (LC) self-assembly is a promising platform to construct nanochannels with various characteristic architectures and coordination geometries.[37–45] The tunable nanostructure and functionality of a LC assembly[37–47] enables it to become an outstanding candidate for the design of nanostructured ion receptors or transporters.[48–59] We previously developed several nanostructured lithium ion-transport materials based on LC assemblies.[59–63] Recently, Sijbesma *et al.* developed sodium and potassium ion-selective nanoporous films upon a templated LC complex.[64] However, lithium ion-selective LC materials have not yet been reported to the best of our knowledge.[37,51,65,66]

Our strategy here is to obtain lithium-selective crown ether (CE) based liquid crystals. A variety of liquid crystals having CE moieties have been prepared.[65–68] Herein we report on the development of nanostructured materials based on LC crown ether receptors for the selective recognition of lithium cations. We designed and synthesized CE derivatives **1**, **2** and **3** with wedge-shaped LC mesogenic parts (Fig. 1).

Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: kato@chiral.t.u-tokyo.ac.jp

† Electronic supplementary information (ESI) available: Experimental details of the synthesis and characterisation of the thermotropic liquid-crystalline properties of all samples. Representative titration spectra and fit binding curves. See DOI: 10.1039/c7sc03652c

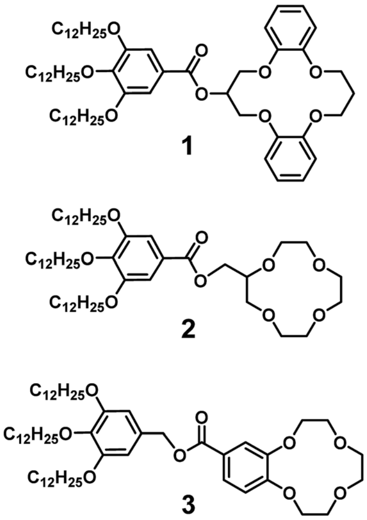

Fig. 1 Molecular structures of liquid-crystalline crown ether receptors: **1** composed of dibenzo-14-crown-4 (DB14C4), **2** composed of 12-crown-4 (12C4) and **3** composed of benzo-12-crown-4 (B12C4).

Results and discussion

Material design

Crown ethers are well-known ionophores towards certain metal ions and their selectivity can be controlled by tuning the number of coordination sites and the cavity size.[69–73] Wedge-shaped crown ether derivatives **1**, **2** and **3** are designed to act as liquid-crystalline ion-selective receptors. The ion-selective moieties of **1**, **2** and **3** consist of dibenzo-14-crown-4 (DB14C4), 12-crown-4 (12C4) and benzo-12-crown-4 (B12C4), respectively (Fig. 1). It is known that the most favourable coordination numbers for lithium cations (Li^+) are expected to be 4, 5 and 6.[74] Additionally 12- to 14-membered CE rings (cavity size: 1.2–1.8 Å) are most selective to Li^+, having an ionic diameter of about 1.4 Å.[15,73,74] Hence, DB14C4 (1.8 Å) is chosen as a selective ligand because of its well matched geometry towards lithium coordination.[75–80] The DB14C4 macrocycle could provide a rigid coordination conformation for ideal Li^+ complexation.[81,82] 12C4 and B12C4 are common and well-known lithium complexing ligands, which have been used to develop lithium-selective materials.[83,84] The introduction of LC mesogenic moieties to the CE derivatives could develop a new class of ion-active LC self-assembled functional materials.[66] Taking advantage of LC self-assembly, liquid-crystalline CE derivatives could form well-defined interconnected ionic channels suitable for selective ion transport.[85–89] Previously, Beginn and co-workers reported LC materials containing sodium ion-selective channels based on the lyotropic LC assemblies of a LC 15-crown-5 derivative and sodium trifluoromethanesulfonate ($NaSO_3CF_3$) in a methacrylate mixture.[90–92] However, LC materials exhibiting lithium-selective properties have not yet been developed. Thus, we considered that the complexation of **1**, **2** or **3** with Li^+ would lead to the development of new, nanostructured lithium ion-selective LC materials (Fig. 2).

Liquid-crystalline properties

The thermal properties of the mesogenic compounds **1–3** and their mixtures with lithium perchlorate ($LiClO_4$) and sodium perchlorate ($NaClO_4$) (1 : 1 equimolar mixture) were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) (see the ESI†). The 1 : 1 mixtures were prepared by adding stoichiometric amounts

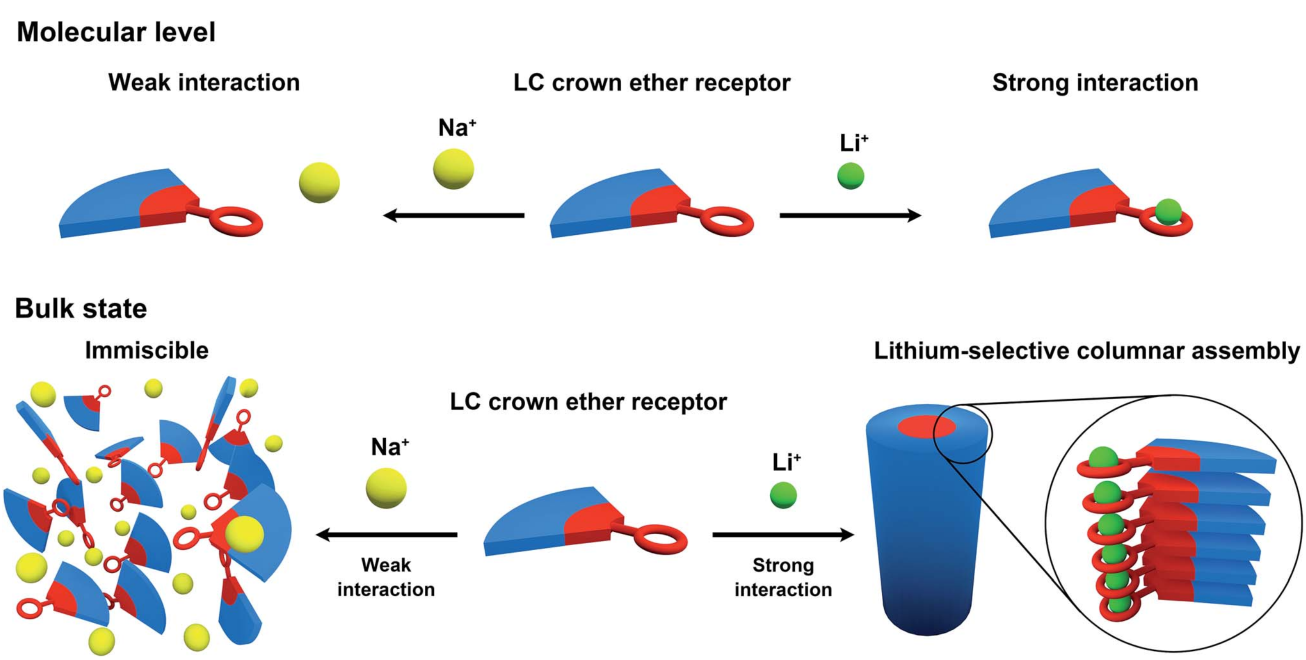

Fig. 2 Schematic illustration of the strategy and material design of liquid-crystalline lithium-selective ion receptors.

Table 1 Thermal properties of compounds **1–3** and equimolar mixtures of **1–3** with $LiClO_4$ or $NaClO_4$

Sample	Phase transition behaviour[a]				
1	Iso	−10	Cr		
1/Li^+	Iso	109	Col_r[b]	73	G
1/Na^+			Phase separation[c]		
2	Iso	2	Cr		
2/Li^+	Iso	156	Col_h	22	Cr
2/Na^+			Phase separation[c]		
3	Iso	14	Cr		
3/Li^+	Iso	−10	Cr		
3/Na^+			Phase separation[c]		

[a] Transition temperatures (°C) were determined by DSC on a first cooling cycle at a scan rate of 10 K min^{-1}. G, glassy; Cr, crystal; Iso, isotropic; Col_r, columnar rectangular phase; Col_h, columnar hexagonal phase. [b] The sample shows monotropic liquid-crystalline Col_r phase upon cooling from the isotropic state. [c] Observed by POM measurements above the isotropization temperature of the single component compounds **1–3**.

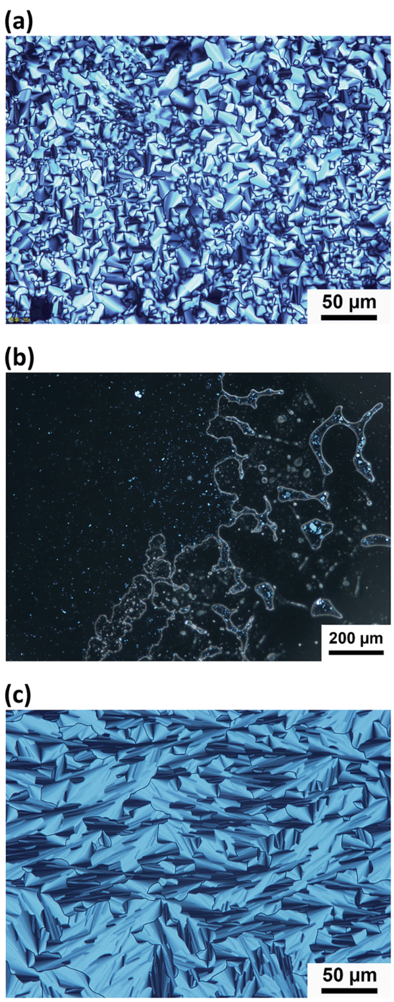

Fig. 3 Polarizing optical microscope images of (a) **1**/Li^+ at 95 °C; (b) **1**/Na^+ at 95 °C and (c) **2**/Li^+ at 130 °C.

of the THF solutions of $LiClO_4$ and $NaClO_4$ to the crown ether derivatives, followed by the complete evaporation of the solvent to yield the anhydrous mixtures.

The phase transition behaviours of the samples are presented in Table 1. Fig. 3 shows the POM images of the mixtures of **1**/Li^+, **1**/Na^+ and **2**/Li^+. The POM images and XRD patterns suggest that complex **1**/Li^+ exhibits a columnar rectangular (Col_r) phase (Fig. 3a and S2†) and complex **2**/Li^+ shows a columnar hexagonal (Col_h) phase (Fig. 3c and S4†). The single components of compounds **1–3** show only crystal and isotropic phases. For **1** and **2**, liquid-crystalline columnar phases are induced after the complexation with $LiClO_4$. The introduction of LC mesophases and significant increases in the isotropization temperatures for both complexes **1**/Li^+ and **2**/Li^+ may be related to the intermolecular ion-dipolar interactions between the CE moieties and lithium cations.[87,89,93] The formation of supramolecular complexes composed of CE moieties and lithium cations may induce well-packed core structures while the aliphatic chains are still mobile. The change in the volume fraction of the polar and nonpolar parts may also contribute to the introduction of LC mesophases. In contrast, $NaClO_4$ salt is immiscible with both compounds **1** and **2**. Liquid–solid phase separations for **1**/Na^+ and **2**/Na^+ are observed above the isotropization temperature by POM measurements (Fig. 3b and S6a†). The DSC thermograms of the mixtures of **1**/Na^+ and **2**/Na^+ are analogous to those of the single components of compounds **1** and **2** (Fig. S1c and S3c†). This observation also suggests that phase separations occur in the mixtures of **1**/Na^+ and **2**/Na^+. It is believed that sufficient supramolecular interactions are essential to generate stable LC phases. Thus, these results imply that the nanostructured lithium-selective ionic channels are formed within the LC assemblies by the selective interactions between Li^+ and the CE moieties.

^{1}H NMR binding studies

Induction of the LC phases has been observed for **1** and **2** by selective interaction with lithium ions. In order to examine the interactions between mesogenic receptors **1–3** and alkali cations (Li^+ and Na^+), ^{1}H NMR measurements of receptors **1–3** treated with excess $LiClO_4$ and $NaClO_4$ in $CDCl_3$/CD_3CN (1 : 1, v/v) solution were performed. Comparison of the ^{1}H NMR spectra of **1**, **2** (Fig. 4) and **3** (Fig. S11†) treated with excess Li^+ and Na^+ reveals the different nature of the interactions between the receptors and the cations. Upon exposure to excess Li^+, all of the related crown ether proton resonances (H_{a-h}) of **1** underwent considerable downfield shifts (Fig. 4a). In contrast, proton resonances H_b and H_{e-h} showed less of a downfield shift in response to the addition of Na^+, while the methylene protons H_c and H_d may exhibit peak splitting (H_{c1}, H_{c2}, H_{d1}, and H_{d2}). This might indicate a weaker interaction between **1** and Na^+, and a conformational change of the DB14C4 ring of **1** (Fig. 4a). The ^{1}H NMR spectra of **2** with Li^+ and Na^+ showed similar but smaller shifts compared to those of **1** (Fig. 4b). Addition of Li^+ induced an apparent downshift movement of H_{a-i} of **2**, and adding Na^+ caused only a slight shift of these proton resonances. However, the ^{1}H NMR

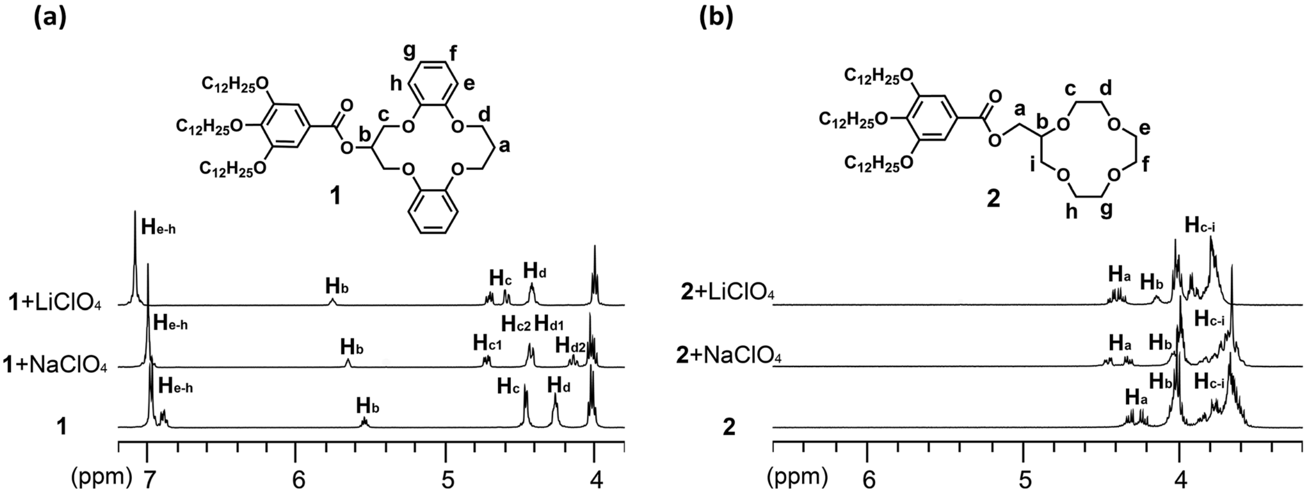

Fig. 4 Partial ^{1}H NMR spectra (400 MHz, 1 : 1 $CDCl_3/CD_3CN$, 298 K) of **1** (a) and **2** (b), showing shifts of the crown ether proton resonances in the presence of excess Li^+ and Na^+.

spectra of **3** showed almost the same downfield shift upon the addition of Li^+ and Na^+ (Fig. S11†). These resonance changes are rationalized in terms of the deshielding and shielding effects that may result from the cation-oxygen atom coordination and conformational changes induced upon different cation complexation.

The abilities of **1**, **2** and **3** to bind lithium and sodium cations in solution were further examined *via* multiple ^{1}H NMR spectroscopic titrations using $CDCl_3/CD_3CN$ (1 : 1, v/v) as solvent (Fig. 5 and ESI†). Cation binding studies of **1**, **2** and **3** were performed by monitoring the shift movement of the respective CE proton resonances upon the addition of Li^+ and Na^+. In all

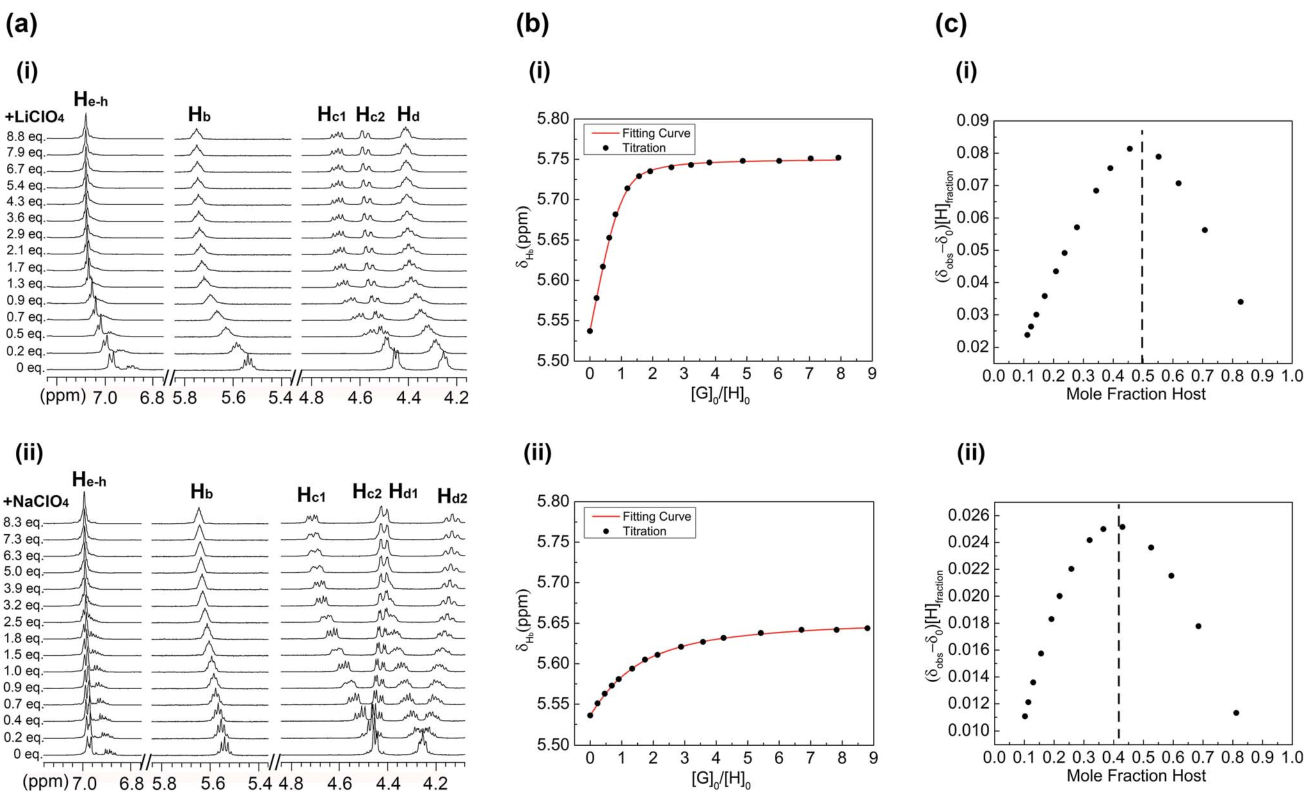

Fig. 5 (a) Partial ^{1}H NMR spectra (400 MHz, 1 : 1 $CDCl_3/CD_3CN$, 298 K) of **1** showing the shifts of the crown ether proton resonances in response to increasing guest concentration (bottom to top) during titrations with (i) $LiClO_4$ and (ii) $NaClO_4$. (b) Representative binding curves obtained by fitting the shifts of the H_b proton resonances against $[Guest]_0/[Host]_0$ from the titrations of **1** with (i) $LiClO_4$ and (ii) $NaClO_4$. (c) Representative Job plots of **1** with (i) $LiClO_4$ and (ii) $NaClO_4$.

Table 2 Association constants, K_a (M^{-1}), of **1**, **2** and **3** towards Li^+ and Na^+ (added as perchlorate salts) in $CDCl_3$: CD_3CN (v/v, 1 : 1) solution at 298 K. All association constants are an average of at least three ^1H NMR titrations fit to a 1 : 1 binding model using BindFit v0.5, and associated errors are <10% unless noted

	Li^+	Na^+	Ion selectivity Li^+/Na^+
1	2359	228	10.35
2	610	377[a]	1.62
3	36	284	0.13

[a] Titrations had errors of <14%.

cases $LiClO_4$ and $NaClO_4$ were used as cation sources. The titrations reveal that the cation-dependent shifting was observed only for the CE related proton resonances. Other ^1H NMR resonances were relatively unaffected by the presence of cationic stimuli.

Table 2 shows the resulting association constants of multiple ^1H NMR spectroscopic titrations that assessed the binding abilities of receptors **1**, **2** and **3** towards Li^+ and Na^+. All binding data were fit to a 1 : 1 binding model and association constants were determined using BindFit v0.5.[94] As shown in Table 2, compounds **1** and **2** exhibit a binding preference for Li^+ over Na^+, while compound **3** shows weak association with both cations and preferentially binds to Na^+ rather than Li^+. Significantly, **1** exhibits a much higher binding ability and ion selectivity for Li^+ than those of **2** and **3**. It displayed association constants of 2359 and 228 M^{-1} towards lithium and sodium cations, respectively. The binding selectivity for Li^+/Na^+ ions is 10.35. As mentioned in the introduction, the effective selectivity of ion-selective ionophores is owed to their characteristic architectures and coordination geometries. The significant preference of **1** for Li^+ could be due to its larger DB14C4 cavity which provides a more ideal geometry for Li^+ coordination, whereas the smaller macrocycles 12C4 of **2** and B12C4 of **3** are less favourable. The high selectivity is achieved by locking the lithium cation into the four oxygen coordination sites around the cavity. The cavity that can fit the cation best is preferred. Moreover, the relatively flexible receptor **2** shows higher binding constants in both cases compared to the rigid receptor **3**. This also implies that the ligand should be flexible enough to allow sufficient ion binding. These results reveal that significant effects on selective binding could be induced by relatively minor structural alterations of the receptors.[93]

Binding conformation investigation

The results of ^1H NMR titration experiments for receptor **1** suggest that Li^+ binding is preferred, as a result of both the preferred coordination number of four and the geometry of the

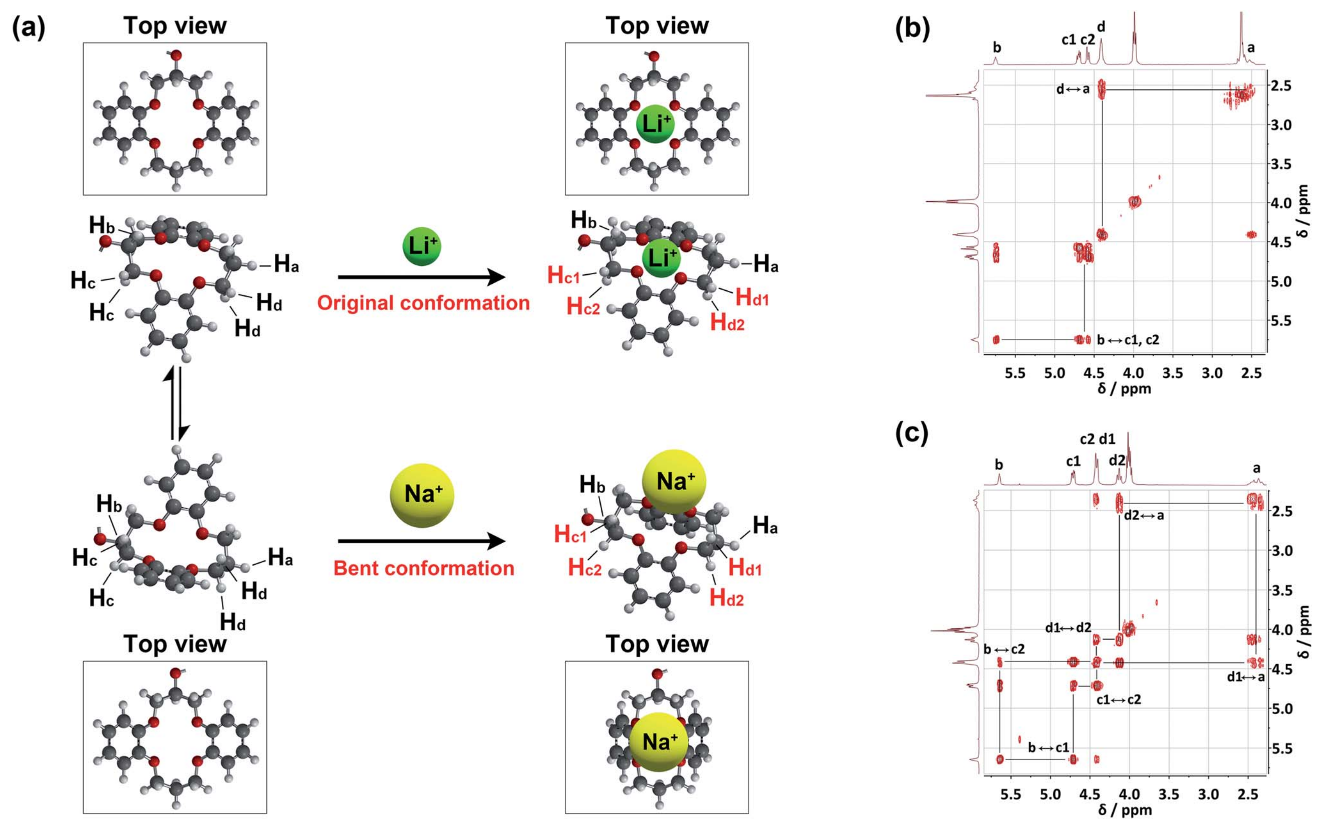

Fig. 6 (a) Schematic illustration of the conformational rearrangements of the DB14C4 part of **1** in response to different guest cations. (b and c) Partial ^1H COSY spectra (400 MHz, 1 : 1 $CDCl_3/CD_3CN$, 298 K) of **1** showing the conformational change of crown ether proton resonances in response to different guest cations (b) **1**/$LiClO_4$ and (c) **1**/$NaClO_4$.

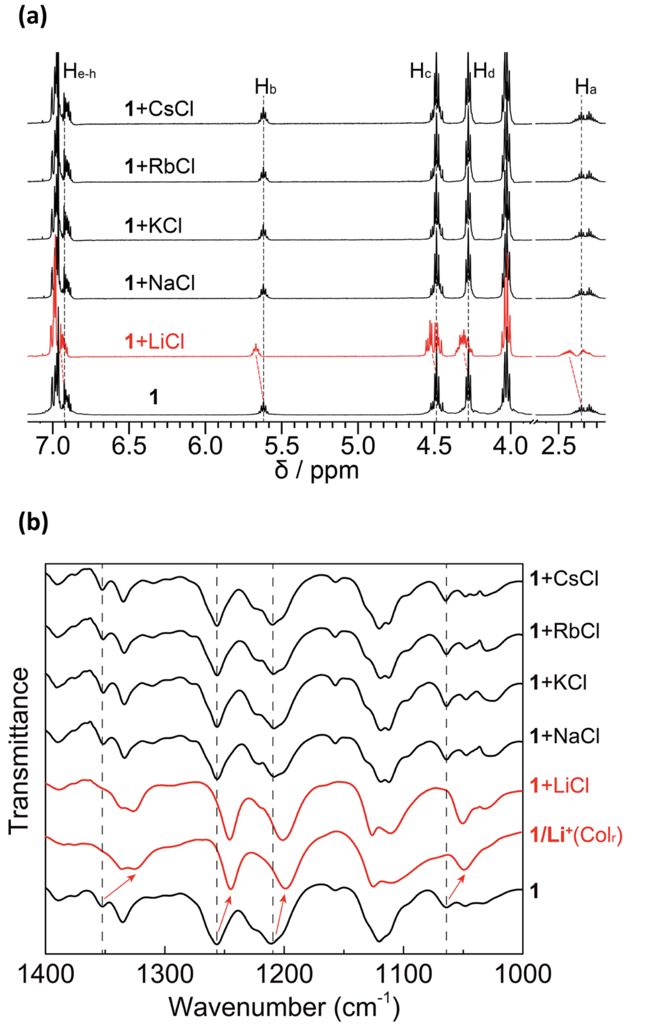

Fig. 7 (a) Partial ^{1}H NMR spectra (400 MHz, 9 : 1 $CDCl_3/CD_3CD$, 298 K) of 5.0 mM solutions of **1** only and **1** with an excess of different alkali metal chloride salts. (b) Partial FT-IR spectra of **1**, **1**/Li^+(Col_r) and **1** mixed with an excess of different alkali metal chloride salts.

DB14C4 cavity (Fig. 5). The analysis of the ^{1}H NMR spectroscopic titration data reveals solution phase structural information about the cationic binding conformations of receptor **1**. In titrations of **1** with Li^+, the related crown ether proton resonances (H_{a-h}) of **1** moved downfield throughout the titrations (Fig. 5a,i). Fig. 5b,i shows that the rapid and noticeable downfield shift almost reached a maximum after adding about 1.0 equiv. of Li^+, then only a slight shift even up to 8.0 equiv. of Li^+. This movement of the CE proton resonances implies the four coordination sites of the DB14C4 ring bind to the lithium cations tightly beyond 1.0 equiv. of Li^+. This can also be confirmed by the Job plot of the titrations (Fig. 5c,i). The peak of the Job plot corresponds to a 0.5 mole fraction of the host in the titration solution, which indicates the formation of a stable 1 : 1 complex of Li^+ and **1**. The DB14C4 macrocycle provides an ideal coordination geometry for Li^+, in which strong supramolecular interactions between the lithium cation and the four ethereal oxygens occur. A different shifting trend was observed for the titrations of **1** with Na^+ (Fig. 5a,ii). The proton resonances (H_{a-h}) of **1** showed not only a downfield shift but also peak splittings and an upfield shift for the methylene protons H_c and H_d. The titration of **1** with Na^+ induced only steady changes in the H_a and H_b resonances up to 9.0 equiv. of Na^+, revealing the weak affinity of **1** towards Na^+ (Fig. 5b,ii). The Job plot of the titrations shows that the equilibrium of the complex formation is at about 0.42 mole fraction of host (Fig. 5c,ii). No stable 1 : 1 complex of Na^+ and **1** was formed according to these results. It is known that Na^+ strongly prefers 6-fold coordination.[34,72] These results imply the four binding sites of DB14C4 are not sufficient to bind larger cations with a higher coordination number. The high selectivity of **1** towards Li^+ is achieved by forming a more stable arrangement of the complex.

The binding conformations of **1** in response to different guest cations were also confirmed by correlation ^{1}H NMR spectroscopy (COSY) (Fig. 6 and S8†). The ^{1}H COSY spectra of **1**/$LiClO_4$ (Fig. 6b) and **1**/$NaClO_4$ (Fig. 6c) reveal the correlations of the DB14C4 proton resonances (H_a, H_b, H_c and H_d), confirming that a conformational rearrangement of the DB14C4 ring occurs upon interaction with a sodium cation. The peak splitting of the methylene protons H_c and H_d is shown in the ^{1}H COSY spectra, this demonstrates a bent conformation of the DB14C4 ring. This suggests that the size of the sodium cation is too large to fit into the DB14C4 cavity. The DB14C4 macrocycle has to be bent to interact with the large sodium cation. A proposed schematic drawing of the conformational rearrangements is shown in Fig. 6a. The DB14C4 ring of receptor **1** in the free state exhibits a rapid interconversion on the NMR timescale between two equivalent conformations.[95] The smaller lithium cation (1.4 Å) can fit easily into the DB14C4 cavity (1.8 Å) (Fig. 6a).[15,73,74] Hence, only the deshielding effects resulting from the lithium cation-oxygen atom interactions were observed for the methylene proton resonances H_c and H_d in the ^{1}H NMR titration and ^{1}H COSY spectra of **1** with Li^+ (Fig. 5a,i and 6b). On the other hand, the interactions with a larger sodium cation (2.0 Å)[15] induces a bent conformation of the DB14C4 ring (1.8 Å) of **1** (Fig. 6a). Not only the deshielding effects from the sodium cation-oxygen atom interactions, but also the shielding effects from the structural changes of the bent conformation, were observed (Fig. 5a,ii and 6c). The methylene proton resonances H_{c2} and H_{d2} thus shift to upfield due to the higher electron density induced by the bent conformation. These results suggest that the high selectivity of receptor **1** for Li^+ results from both the preferred coordination number of four and the favoured geometry of the DB14C4 cavity.

Lithium selectivity over other alkali metal chloride salts

In order to evaluate the lithium-selective binding ability of **1** towards different alkali metal chloride salts in solution, ^{1}H NMR measurements of **1** with excess alkali chloride salts were performed using a mixture of $CDCl_3$ and CD_3OD (9 : 1, v/v) as the solvent (Fig. 7a). Exposing **1** to excess LiCl induced distinctive changes in the ^{1}H NMR spectrum. These changes in the DB14C4 proton resonances (H_{a-h}) are analogous to those seen in the titrations with $LiClO_4$. In contrast, no appreciable chemical shift changes were observed in the ^{1}H NMR spectra of the same solutions of **1** after exposure to excess NaCl, KCl, RbCl and CsCl, even after leaving overnight. We conclude that **1** is capable of binding LiCl with high selectivity over other alkali salts in the solution state.

The selective interactions between **1** and LiCl were also examined by FT-IR measurements in the solid state. After mixing **1** with excess LiCl, NaCl, KCl, RbCl and CsCl salts in CH_3Cl/CH_3OH (9 : 1, v/v) solution, the solvent was removed completely under reduced pressure and the resulting mixtures were dried and analysed with FT-IR spectroscopy (Fig. 7b). Only the mixture with LiCl showed shifts in the ester and ethereal C–O stretching vibration bands from 1355, 1258, 1211 and 1062 cm^{-1} to 1328, 1246, 1201 and 1047 cm^{-1}, respectively. These shifts to lower wavenumbers are attributable to the formation of a complex between **1** and Li^+ that causes more restriction in the C–O vibrations of the DB14C4 cavity. In contrast, none of the other alkali cations showed interactions with **1**. FT-IR measurement was also performed on **1**/Li^+ at 95 °C in Col_r LC phase, which is denoted as **1**/Li^+(Col_r). The IR spectrum of **1**/Li^+(Col_r) is analogous to that of **1** + LiCl. The LC nanostructure has a minor negative effect on the selectivity of **1** towards lithium ions. These results demonstrate that the selective lithium-ion interactions of **1** towards LiCl in the solid state are the same as those of **1**/Li^+ in LC assembly.

Conclusions

In conclusion, we developed nanostructured LC materials, formed by the co-assembly of wedge-shaped CE derivatives (**1** or **2**) and $LiClO_4$. To the best of our knowledge, compounds **1** and **2** are the first lithium ion-selective receptors capable of forming stable LC nanostructures. The system we reported here can be applied to the fabrication of various LC-based ion-recognition materials, and opens new pathways for the development of new techniques for efficient lithium-selective extraction. It is shown that the self-assembly of the LC columnar structures is driven by the selective supramolecular interactions between the CE moieties and lithium cations. The lithium selectivity of the compounds was characterized by ^{1}H NMR and FT-IR spectroscopy. Remarkably, compound **1** with a DB14C4 moiety shows high selectivity towards lithium salts over the corresponding alkali metal salts. We have found that the high selectivity of **1** for Li^+ is due to the preferred coordination number of four and the ideal cavity geometry of the DB14C4 moiety.

Experimental

The synthesis and characterization of compounds **1–3** are described in the ESI.†

Preparation of the mixtures

Compounds **1–3**, $LiClO_4$ and $NaClO_4$ were dried under vacuum at 60 °C for at least 8 h before the preparation. All the materials and solvents for the preparation of the mixtures were dried before use. Mixtures of the receptors and salts were prepared by adding the appropriate volume of a THF solution of $LiClO_4$ or $NaClO_4$ (0.056 M) to a weighed amount of CE derivatives **1**, **2** and **3** (10–20 mg) in a microtube. The solution was homogeneously dispersed by sonication and then the solvent was slowly removed by rotary evaporation. The samples were dried under vacuum at 60 °C for 8 h before their study.

NMR titrations

A 5 mM host stock solution of respective receptors **1**, **2** or **3** was prepared using a mixture of $CDCl_3$ and CD_3CN (1 : 1, v/v) as the solvent. The guest stock solutions (100 mM) were prepared by dissolving respective alkali metal salts using the as-prepared host stock solutions as the solvent to maintain a constant host concentration throughout the titration. In each titration, 500 μL of the host solution was transferred to an NMR tube *via* a Hamilton gas tight microsyringe. An appropriate volume of the guest solutions was added *via* a Hamilton gas tight microsyringe to the host solution in the NMR tube for titration, and a spectrum was obtained *via* a JEOL JNM-ECX400 NMR spectrometer at 298 K after thorough mixing. Association constants (K_a) were calculated by non-linear curve fitting of the obtained titration isotherms fit to a 1 : 1 binding model using BindFit v0.5.[94] The reported association constants were calculated from the downfield shifting of all of the distinguishable related crown ether proton resonances for cation titrations. All titrations were performed at least in triplicate.

Conflicts of interest

There are no conflicts to declare.

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