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Derivatives of 14-Crown-4 – Tuning the Selectivity to Lithium for Detection and Extraction

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Nowadays, lithium is a critical element essential for the production of lithium-ion batteries, as well as for use in glass and ceramics manufacturing, lubricants, metallurgy, and the nuclear industry. The continuously growing industrial demand for lithium drives the development of efficient techniques for its extraction from a wide range of sources – from natural salines to industrial wastes. Since the global lithium reserves are mostly dispersed in seawater in vanishing concentrations, the extraction is the most promising technique for its isolation. In turn, crown ethers provide opportunities for the precise tuning of their physical-chemical properties, allowing to control coordination properties, solubility and selectivity for particular metal ions through chemical modification. Despite the relatively little reported studies, crown ethers of 14-crown-4 type can be considered as a promising platform for the development of selective extractants of lithium for further development of industrial extraction processes. The present review is aimed to systematically analyze the existing data concerning the aspects of synthesis and application of 14-crown-4 derivatives for the detection and extraction of lithium.

Keywords: Crown ethers, 14-crown-4, lithium, extraction.

Производные 14-краун-4-эфира – пути настройки селективности для детектирования и экстракции лития

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В настоящее время литий является критически важным элементом для производства литий-ионных аккумуляторов, а также для использования в производстве стекла и керамики, смазочных материалов, металлургии и атомной промышленности. Постоянно растущий спрос на литий инициирует разработку эффективных методов его извлечения из широкого спектра источников – от природных рассолов до промышленных отходов. Поскольку мировые запасы лития преимущественно сосредоточены в морской воде в крайне низких концентрациях, экстракция является наиболее перспективным методом его выделения. В свою очередь, краун-эфиры предоставляются удобными объектами, предоставляющими возможности для управления путем химической модификации их физико-химическими свойствами, такими как координационные свойства, растворимость и селективность по отношению к определенным ионам металлов. Несмотря на относительно небольшое количество исследований, краун-эфиры типа 14-краун-4-эфира можно рассматривать как перспективную платформу для разработки селективных экстрагентов лития для дальнейшего развития промышленных экстракционных процессов. Целью настоящего обзора является систематический анализ литературных данных, касающихся синтеза и применения производных 14-краун-4-эфира для детектирования и извлечения лития.

Ключевые слова: Краун-эфиры, 14-краун-4, литий, экстракция.

Introduction

Lithium has undoubtably become a crucial element for humanity due to its broad range of applications in various fields including metallurgy, ceramics and heat-resistant lubricants. Lithium-ion batteries are occupying a special place among these technologies, as they are currently indispensable for powering a huge array of wireless electronic devices. The 2019 Nobel Prize in Chemistry was awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino for their contributions to the development of the lithium-ion battery, thus highlighting the impact of lithium-based energy sources on our civilization.

It is expected that the demand on lithium will continue to grow for next decades,[1,2] thus the depletion of economically viable lithium sources may constrain its widespread use.[3] In this context, investigation of other lithium sources is necessary to fullfill the constantly growing demand. The estimated reserves of lithium in seawater are exceeding the reserves on land by at least an order of magnitude,[4] albeit it is evenly distributed in water at sub-ppm concentrations.[5] In addition, high Mg/Li ratio and the presence of other ions posing a significant challenge for its extraction. Despite the mentioned difficulties, seawater offers virtually unlimited source of lithium. In this respect the development of novel selective extractants for efficient removal of lithium from seawater is a worthwhile objective.

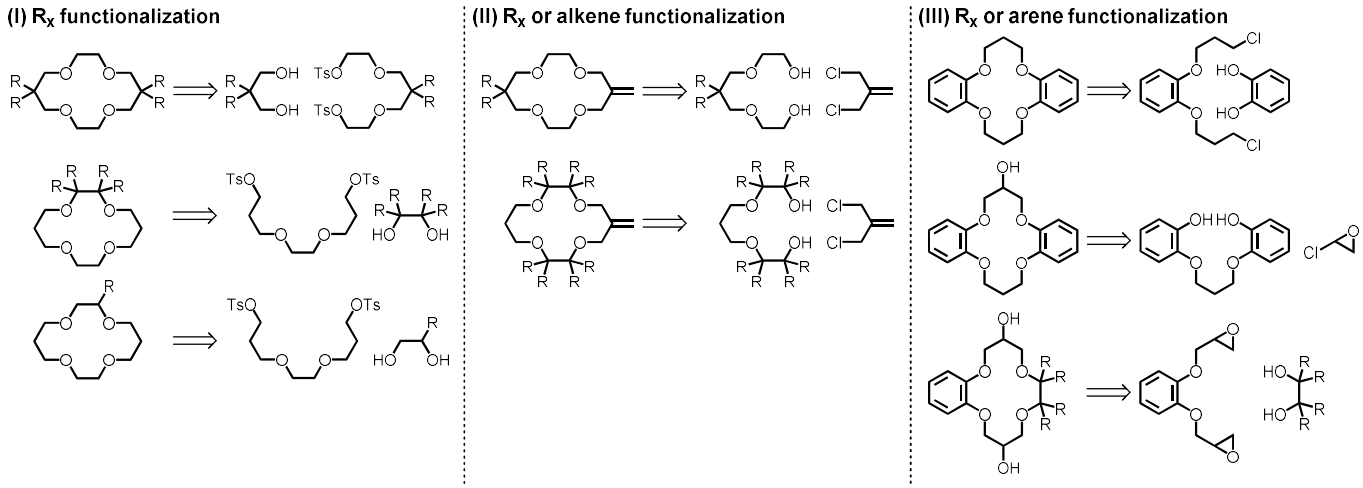
Crown ethers of 14-crown-4 type are known to selectively extract lithium from water even in the presence of interfering ions.[6] Despite the relatively low number of reports related to these molecules, 14-crown-4 ethers is a promising class of compounds for extraction of lithium. In the present review we systematically analyzed the existing data about synthetic approaches towards various 14-crown-4 ethers and its extraction properties with special attention to lithium selectivity in the presence of interfering ions. In addition, extraction systems and hybrid materials based on 14-crown-4 ethers were also discussed. Conformational analysis of some ethers using X-ray diffraction and NMR spectroscopy was also considered as a valuable tool for elucidating the mechanisms of lithium coordination.

Synthesis

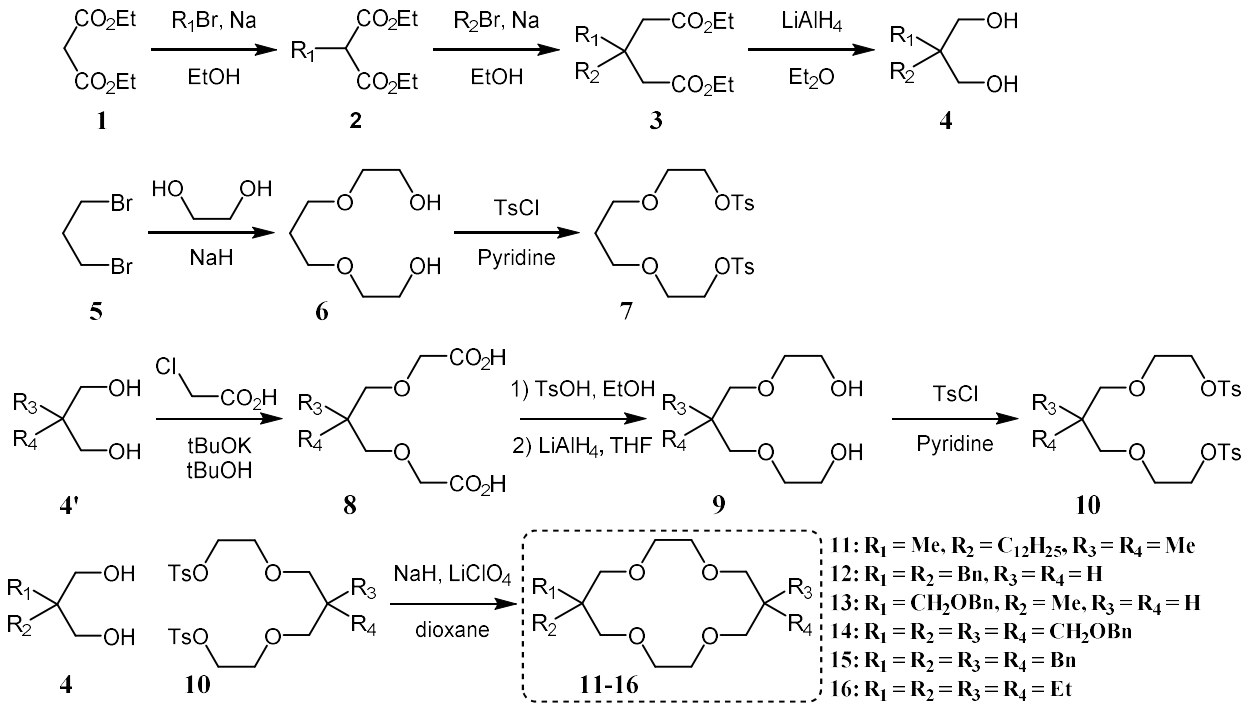
Crown ethers are usually synthesized by macrocyclization of diols with corresponding ditosylates or with organic chlorides. The sequential alternate introduction of C_2 and C_3 building blocks is a general route towards substituted 14-crown-4 ethers (Scheme 1). Commonly utilized synthetic pathways were divided into 3 categories in Scheme 1 for clarity. Preliminary functionalization of C_2 or C_3 building blocks before macrocyclization affords crown ethers with various substitution patterns. Alkyl substituents with desired functional groups can be introduced in the ether skeleton using the described methodology. In addition, molecules containing alkene fragments can be also used for macrocyclization reaction giving corresponding ethers suitable for further post-modification of double bond. Besides that, numerous benzo- and dibezo-14-crown-4 ethers are known. Unlike other ethers, benzo- and dibenzo-14-crown-4 derivatives have relatively rigid structure due to the presence of benzene rings. These aryl fragments can be also modified to control complexation properties and solubility in water and organic media.

As it can be seen from Scheme 1, currently existing synthetic protocols and their combinations allow to obtain desired 14-crown-4 ethers with virtually any substitution pattern. More detailed consideration of the existing synthetic methods will be discussed further.

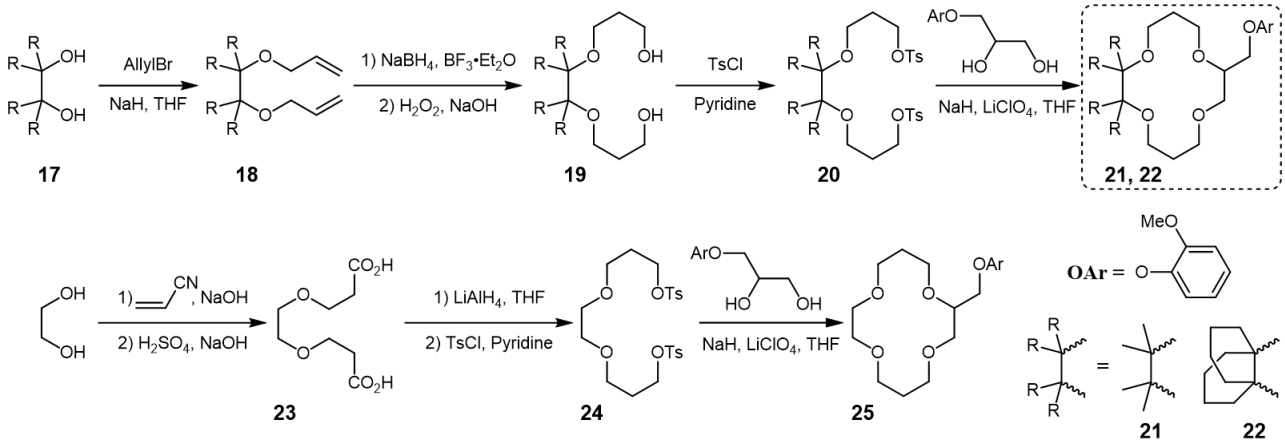
Construction of substituted C_3 building blocks greatly relies on the chemistry of malonate esters (Scheme 2). Alkylation of diethyl malonate **1** typically gives disubstituted product **3** ($R_1 = R_2$), though monoalkylation which gives product **2** is known in case of long-chain linear alkyl bromides.[7,8] In this respect alkyl malonate **2** can be converted to dialkyl malonate **3** with two different substituents ($R_1 \neq R_2$) or used as is for further transformations. Reduction of malonate ester **3** with lithium aluminum hydride produces substituted diol **4**. The obtained diol can be used for macrocyclization with ditosylate, though construction of the second building block should be considered.



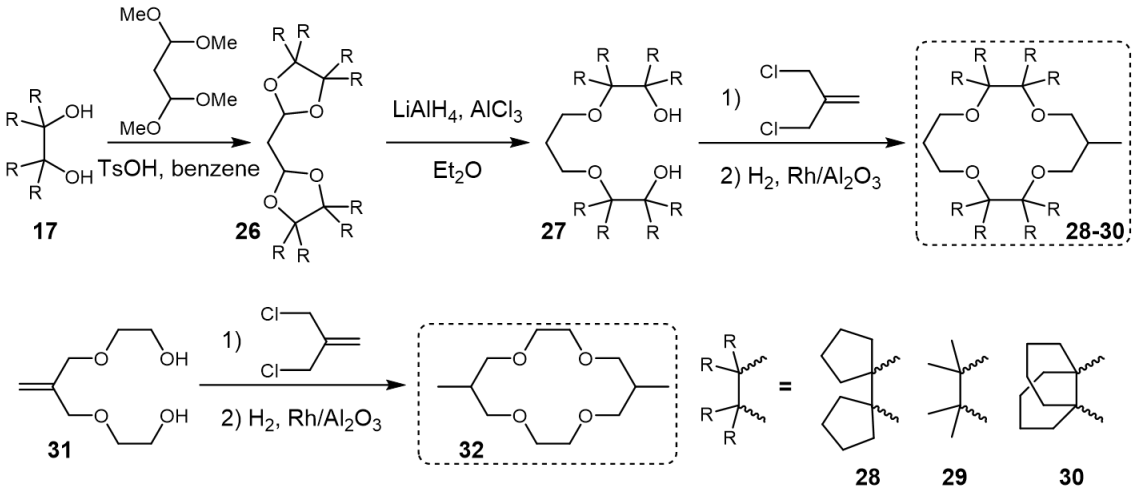
Scheme 1. General synthetic routes towards 14-crown-4 derivatives.



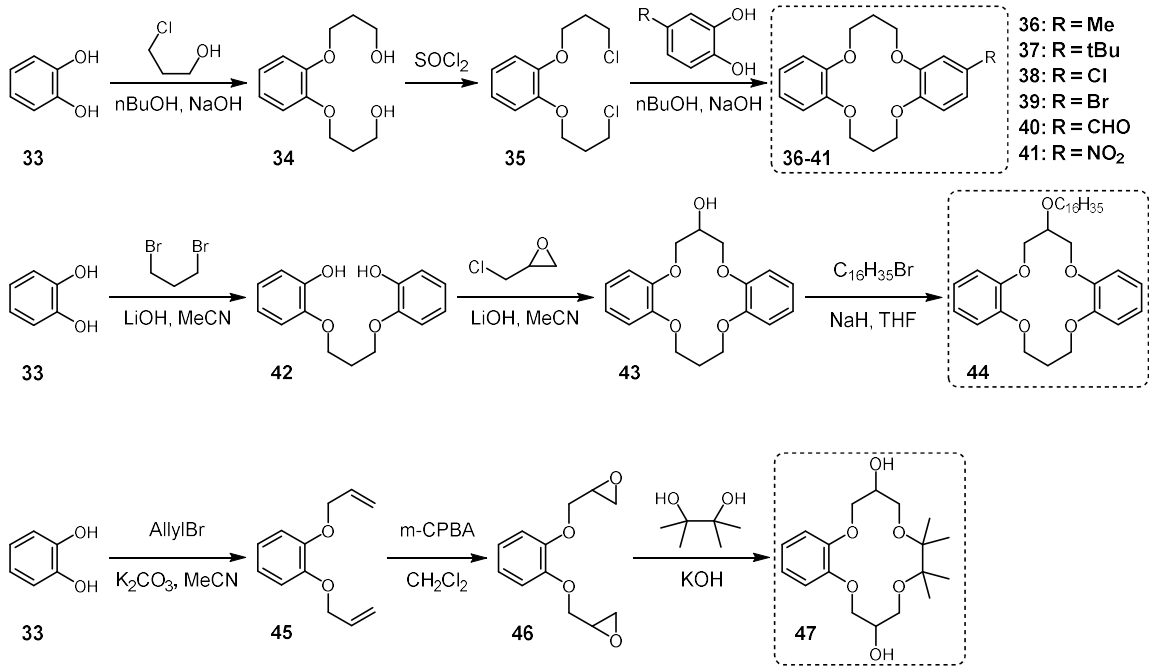
Scheme 2. Construction of functionalized C_3 building blocks for the synthesis of corresponding ethers with various substituents.



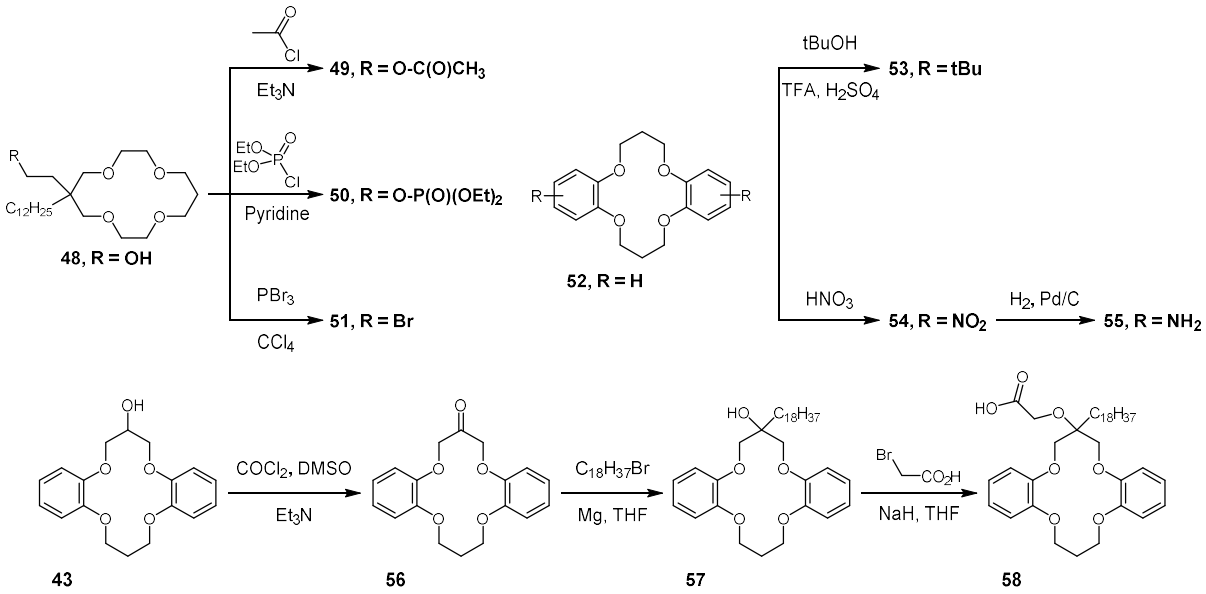
Scheme 3. Functionalization of C_2 building blocks for crown ether synthesis.



Scheme 4. Synthesis of 14-crown-4 ethers bearing double bonds and an example of post-modification.



Scheme 5. Synthesis of benzo- and dibenzo-14-crown-4 ethers.



Scheme 6. Various examples of post-modification of 14-crown-4 derivatives.

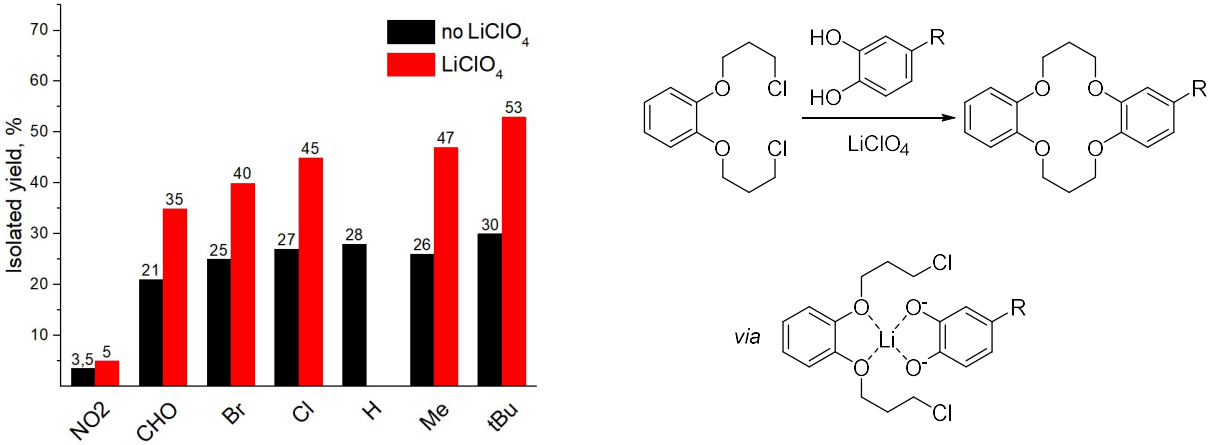


Figure 1. Template effect in the synthesis of dibenzo-14-crown-4 derivatives; no yield was provided for the synthesis of dibenzo-14-crown-4 in the presence of $LiClO_4$.

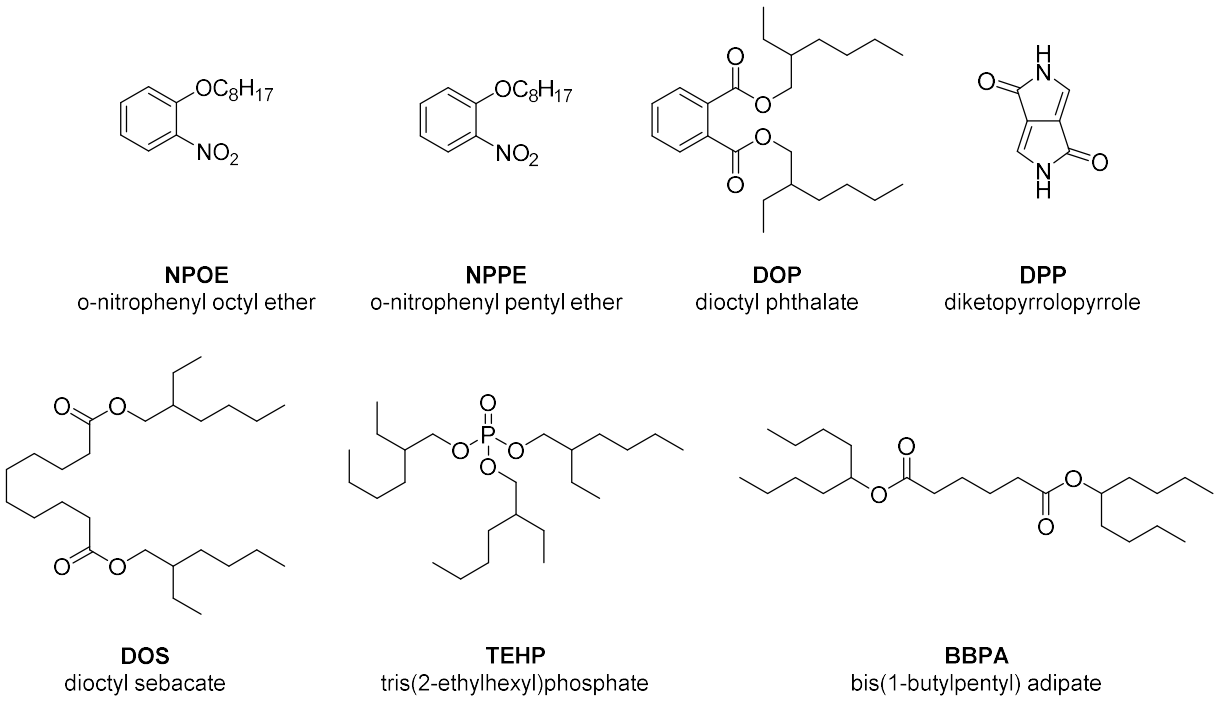


Chart 1. Structure, name and abbreviations of membrane solvents mentioned in the current topic.

Unsubstituted ditosylate **7** can be prepared from 1,3-dibromopropane **5** by reaction with ethylene glycol and subsequent tosylation.[9] Substituted ditosylate **10** can be obtained *via* 3 steps from functionalized diol **4'** (the apostrophe symbol is used to specify the difference from diol **4**). Alkylation of chloroacetic acid with diol **4'** in the presence of base affords product **8**. Esterification and reduction sequence gives molecule **9** with functionalized C_3 unit. Finally, tosylation affords ditosylate **10**. Macrocyclization of diol **4** with ditosylate **7** or **10** produces the desired functionalized 14-crown-4 ether.

Another way to functionalize 14-crown-4 ethers consists in modification of C_2 building block and thus various 1,2-diols are widely used for this purpose.[10,11] Low symmetry 14-crown-4 ethers can be prepared according to Scheme 3. Substituted diol **17** can be alkylated with allyl bromide giving ether **18**. The product can react with *in situ* generated diborane to produce **19**. Subsequent tosylation and substitution give crown ethers **21** and **22**, respectively.

Slightly different route can be used to obtain crown ether **25** from ethylene glycol. Conjugate addition to acrylonitrile and hydrolysis allow to obtain compound **23**. Reduction and tosylation give product **24** which is similar to previously discussed precursor **20**. Analogously, substitution gives crown ether **25**.

An elegant approach towards C_2-functionalized symmetrical 14-crown-4 ethers is shown in Scheme 4.[12] Diol **17** reacts with 1,1,3,3-tetramethoxypropane so more thermodynamically favorable cyclic acetal **26** is formed. Next, the acetal **26** is cleaved with strong reductant to form molecule **27** bearing functionalized C_2 units. Interaction with unsaturated organic chloride gives 14-crown-4 derivative with double bond at C_3 building block.[13] Catalytic hydrogenation of the product affords ethers **28-30**. Molecule **31** can be used instead of **27** to produce ether with 2 alkene fragments and its hydrogenated product **32**.

Synthetic methods towards benzo- and dibenzo-14-crown-4 ethers slightly differ from the protocols discussed above (Scheme 5). Catechol **33** and its derivatives are typically used as synthons for the synthesis, thus monosubstituted dibenzo-14-crown-4 ethers **36-41** can be prepared from catechol.[14] Alkylation of the hydroxyl-groups with an excess of 3-chloropropanol gives product **34**. Attached hydroxyl-groups can be replaced with chlorine atoms upon treatment with thionyl chloride. Reaction of **34** with substituted catechols gave ethers **36-41**, that allowed preparation of a library of these compounds with various substituents.

Catechol **33** is also able to react with 1,3-dibromopropane providing molecule **42**.[15] Dropwise addition of 1,3-dibromopropane ensures formation of the desired product. Further reaction with epichlorohydrin gives product **43** *via* epoxide opening and S_N2 substitution of chlorine atom. The unprotected hydroxyl-group can be modified with various alkylating agents, *e.g.*, alkyl bromide, forming compound **44**. Reaction between pyrocatechol **33** and allyl bromide affords product **45** in a similar way as aliphatic diols.[16] The available terminal double bonds can be epoxidized with *m*-CPBA to give **46**. Both epoxide fragments are opened with pinacol to give ether **47**.

Post-functionalization of peripheral substituents serves as another way for tuning physico-chemical properties of crown ethers (Scheme 6). Thus, *tert*-butanol can be used as a reagent to produce **53** from **52** under acidic conditions.[17] Dibenzo-14-crown-4 can be converted into **54** *via* nitration reaction and the product can be hydrogenated to give **55**.[18]

Acylation of hydroxy-group of **48** with acyl chloride and diethyl phosphorochloridate, substitution of the hydroxyl group with bromine was successfully performed.[7] Hydroxy-group can be transformed to ketone that was demonstrated for dibenzo-14-crown-4 derivative **43** under Swern oxidation conditions.[19] Addition of Grignard rea-

gent provided **57** which was further alkylated with bromoacetic acid to yield **58**.

Macrocyclization reaction is mostly conducted in the presence of $LiClO_4$. A template effect of the Li^+ cation was discussed in case of dibenzo-14-crown-4 ethers[14] and the increased of yield was demonstrated in the synthesis of some dibenzo-14-crown-4 derivatives in the presence of $LiClO_4$ (Figure 1). The relative increment of yield was at least 30%. The authors also mention that introduction of electron-donating substituents in benzene rings increased relative increment of yield, in contrast to electron-withdrawing groups. The provided explanation is that electron-withdrawing substituents disperse the charge density on oxygen atoms so the Li-O ion-dipole interaction weakens.

Extraction properties

Selectivity diagrams for PVC membranes containing 14-crown-4 derivatives

Polymer membrane ion-selective electrodes are widely used for detection of various anions and cations in solution.[20–22] The measurements of electromotive force (EMF measurements) of polymeric membranes containing ionophore proved to be a convenient tool for determination of selectivity coefficients of crown ethers. The Nikolsky-Eisenman equation[23] is widely used to evaluate selectivity of crown ethers to complexation reaction. This empirical equation can be written as follows:

$$E = E_0 - 2.303\frac{RT}{z_i F}\log(a_i + K_{ij}a_j^{z_i/z_j}), \qquad (1)$$

where E is the measured electrode potential, E_0 – standard potential of the electrode, a_i – activity of the primary ion, a_j – activity of the interfering ion, z_i and z_j are the charges of corresponding ions and K_{ij} – selectivity coefficient for the interfering ion relative to the primary ion. The latter coefficient is also called ion selectivity factor.

Typical fabrication procedure of polymeric membrane[24] includes mixing of ionophore (*ca*. 1-10% by weight), membrane solvent (more than 50% by weight) and PVC matrix (*ca*. 30-40% by weight). Membrane solvents mentioned in the present review are listed in Chart 1.

In addition, potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB) is often added in the mixture (*ca*. 10-50 mol% relative to ionophore). This compound is known to reduce the membrane resistance and suppress permeation of counteranions in aqueous phase into the membrane phase.[9] Reported data also show longer response times and severe EMF drift in the absence of KTpClPB.[25] Besides that, addition of the lipophilic salt may also increase selectivity towards Li^+ cation of 14-crown-4 derivatives.[26]

Comparison of selectivity factors of 14-crown-4 derivatives impregnated in PVC matrices is a helpful tool to evaluate structural factors responsible for selectivity towards specific cations. Figure 2 shows selectivity factors for some 14-crown-4 derivatives.[27] It can be clearly seen that all the shown 14-crown-4 derivatives can selectively bind Li^+ cation, though dibenzo-14-crown-4 possesses less selectivity compared to aliphatic 14-crown-4 ethers. On the other hand, this feature can possibly be used for extraction of alkali metals from liquid phase in the presence of other ions. Group 2 metals bind with all these ethers much weaker ($\log(k_{Li,J})$ is more than 4 orders of magnitude lower compared to Li^+). Interestingly, introduction of bulky aliphatic substituents can notably increase selectivity towards lithium. It can be attributed to conformational changes of macrocyclic structure induced by the presence of aliphatic substituents.

Figure 3 shows the influence of peripheral oxygen-containing functional groups on the selectivity of dibenzo-14-crown-4 ethers.[28] Introduction of peripheral coordinating sites strongly decreases the selectivity towards lithium. Even group 2 metals can compete for the coordination center. It is known that the size of cavity in the 14-crown-4 structure ensures decent selectivity towards Li^+ cation.[29] Introduction of peripheral coordinating site may reduce the selectivity due to the axial coordination of ions with bigger size.

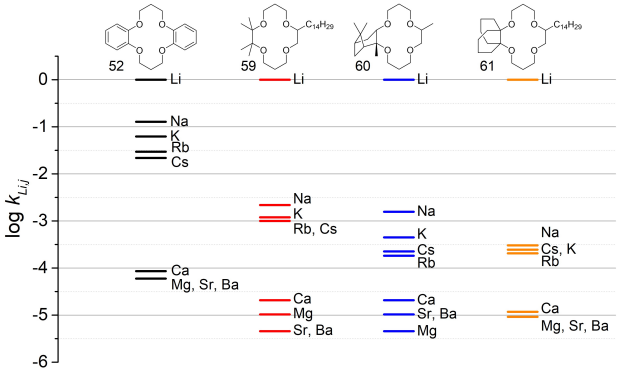


Figure 2. Selectivity factors $\log(k_{Li,j})$ for PVC membranes containing various 14-crown-4 derivatives; NPOE was used as a membrane solvent; The membranes contained KTpClPB; The given selectivity factors $\log(k_{Li,j})$ are measured separately for each compound.

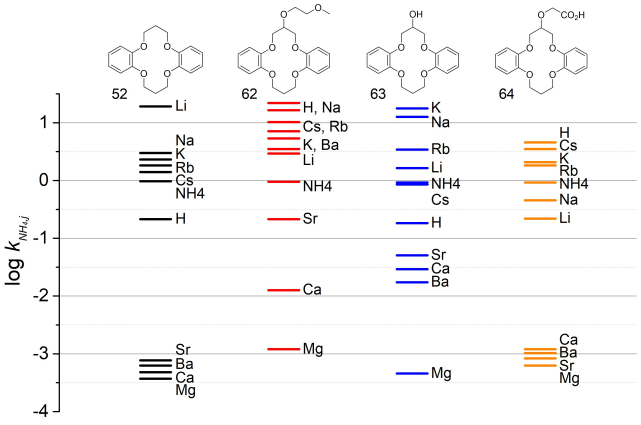


Figure 3. Selectivity factors $\log(k_{NH4,j})$ for membranes containing dibenzo-14-crown-4 derivatives; DOS was used a membrane solvent; The membranes contained KTpClPB; The given selectivity factors $\log(k_{NH4,j})$ are measured separately for each compound.

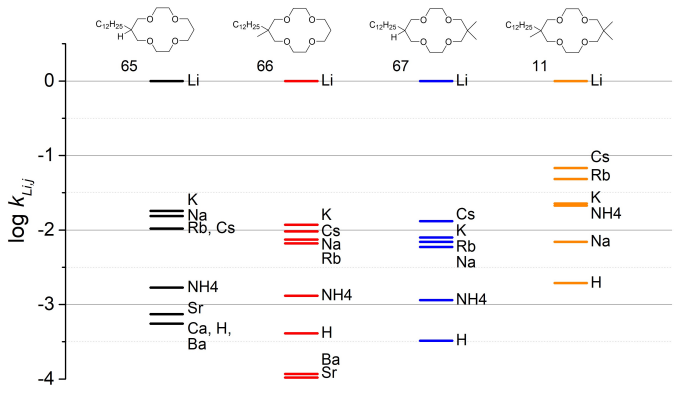


Figure 4. Selectivity factors log($k_{Li,j}$) for PVC membranes containing various aliphatic 14-crown-4 derivatives; NPOE was used as a membrane solvent; The membranes contained KTpClPB; The given selectivity factors log($k_{Li,j}$) are measured separately for each compound.

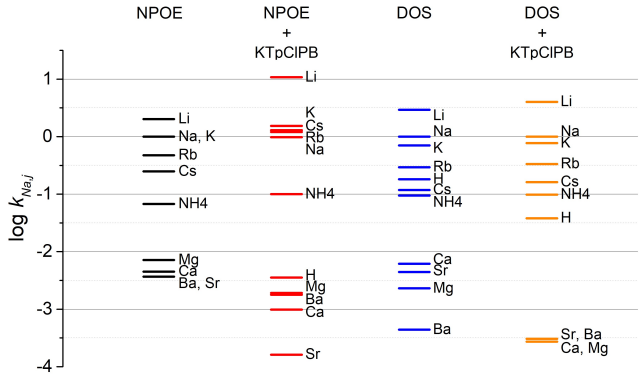


Figure 5. Selectivity factors log($k_{Na,j}$) for PVC membranes containing dibenzo-14-crown-4 ether **52**; NPOE and DOS in the presence and in the absence of KBTpClB were used as membrane solvents.

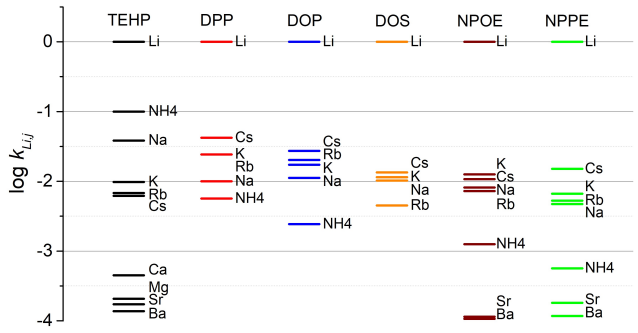


Figure 6. Selectivity factors log($k_{Li,j}$) for PVC membranes containing dodecylmethyl 14-crown-4 ether **66** in various membrane solvents; The membranes contained KTpClPB.

The conformation of all DB14C4 complexes is presumed to be similar based on X-ray data,[30,31] therefore difference in selectivity should be explained by side arm functional groups. According to the reported data,[29,32,33] Li^+ prefers square-pyramidal geometry when occupying 14-crown-4 coordination center. Indeed, dibenzo-14-crown-4 ether provides suitable geometry for coordination (apical coordination site is occupied by counterion or water molecule). In ether **63** the hydroxyl group probably gives rise to proton binding so encapsulated water molecule may hinder coordination of metal ions which explains poor selectivity. Ether **62** and **64** have too short side arms which can't bring the oxygen atom into a proper apical position for Li^+ coordination. In contrast, these side arms are flexible enough to allow participation in six- to eight-coordination binding of larger cations.

A small change in the nature of aliphatic substituents can also notably affect the coordination properties.[9] As it can be seen from Figure 4, the selectivity is affected not only by the number of methyl groups but also by their position in the macrocycle. The selectivity of these compounds is higher compared to dibenzo-14-crown-4 ethers, though ethers with functionalized C_2 building block possess even slightly higher selectivity (Figure 2).

The selectivity factors ought to be independent from the neutral carrier concentration in the membrane if both considered ions form 1:1 complex with ionophore.[9] The latter statement is true for **64**, however ether **63** showed notable decrease of selectivity towards Li^+ compared to Na^+ and K^+ upon increase of its concentration. This finding suggests that the ether **63** is able to form sandwich-type complex with Na^+ and K^+ with 2:1 stoichiometry of crown ether and ions as well as with 1:1 stoichiometry, while ether **64** is able to form only 1:1 complex. The conclusions are also supported by previous research articles of the group – the authors demonstrated that bis(crown ether)s generally show enhanced selectivity towards bigger ions compared to mono(crown ether)s with the same size of macrocycle due to formation of sandwich-type complexes.[34–36] The phenomenon can be explained with formation of 2:1 complexes of bis(crown ether)s with metal ions, thus the concentration dependence of selectivity factors of ether **63** is likely due to the formation of sandwich-type complexes.

The nature of membrane solvent and the presence of lipophilic salt KTpClPB also affects extraction properties of crown ethers.[26] This peculiarity was studied for dibenzo-14-crown-4 ether (Figure 5). Addition of KTpClPB distinctly increased selectivity towards lithium, while the nature of the solvent also affected the selectivity. The authors showed that proper selection of membrane solvent drastically increases selectivity, e.g., switching from DOS to NPOE in the presence of KTpClPB.

The observed strong influence of lipophilic salt on the selectivity factors was explained by the same authors. In water and other highly solvating media, the cationic complex and anion are separated, thus no anion effect is observed. In contrast, membrane solvents solvate ions poorly, therefore the ion pairing occurs. Obviously, electrostatic cation-anion interaction depends on the nature of anion. Consequently, lipophilicity of the anion is important for the dissolution of complex in low polar membrane solvents. One may notice that the lipophilic salt KTpClPB is widely used for the study of selectivity factors for PVC membranes.

Next, the nature of membrane solvent was thoroughly studied by Kitazawa *et al.*[25] for dodecylmethyl 14-crown-4 ether (Figure 6). As it was stated above, proper selection of membrane solvent is crucial for preparation of ion-selective electrodes. The phosphate-based membrane solvent TEHP showed the worst Li^+ selectivity, while in the

membranes with diester-type solvents, namely, DPP, DOP and DOS, Li^+ selectivities are similar. Phenyl ether-type solvents NPOE and NPPE demonstrated superior selectivity over alkali metal ions compared to the diester-type solvents and TEHP. However, the Li^+ selectivity over alkaline-earth metal ions showed the opposite trend between diester- and phenyl ether-type solvents. Presumably, it could be partly due to the difference in the dielectric constants of the two types of solvents.

In contrast, ion selectivity of decalino-14-crown-4 ether was less susceptible to the nature of membrane solvent.[37] Figure 7 shows selectivity factors for PVC membranes containing decalino-14-crown-4 ether. This compound possesses high selectivity towards lithium and variation of membrane solvents didn't significantly change the selectivity, although solvents with low polarity (BBPA and BEHP) showed slightly higher selectivity over Na compared to polar solvents such as NPOE and NPPE.

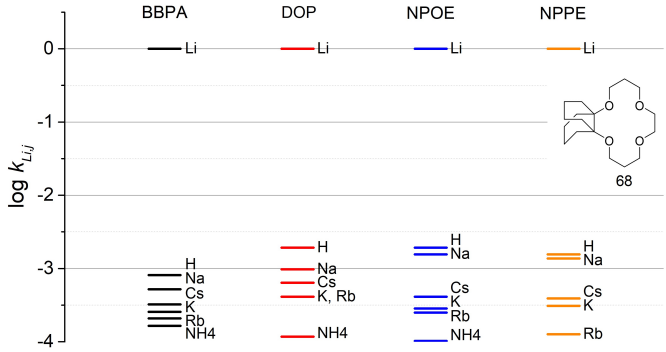


Figure 7. Selectivity factors log($k_{Li,j}$) for PVC membranes containing decalino-14-crown-4 ether **68** in various membrane solvents; the membranes contained KTpClPB.

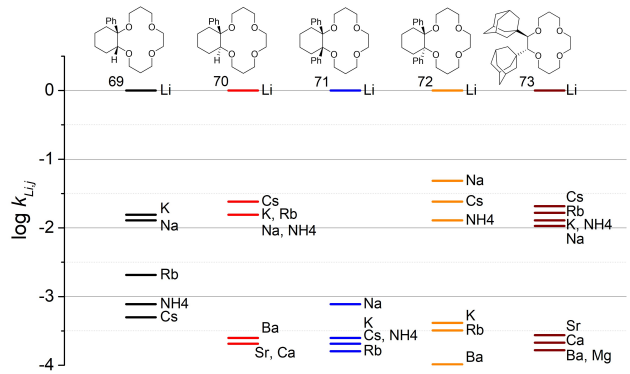


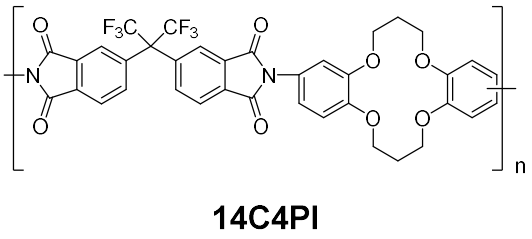
Figure 8. Selectivity factors log($k_{Li,j}$) for PVC membranes containing enantiopure 14-crown-4 derivatives; BBPA was used as a membrane solvent; The membranes contained KTpClPB; The given selectivity factors log($k_{Li,j}$) are measured separately for each compound.

An interesting research about extraction properties of enantiopure 14-crown-4 derivatives was published by Tobe and co-authors.[11] Several stereoisomers were prepared and their selectivity factors were found (Figure 8). It can be seen that *cis* isomers showed higher Li^+ selectivity compared to their *trans* isomers (**69** and **70**; **71** and **72**, respectively). The authors conducted MM3* calculations along with the analysis of available X-ray data to get insights into the relationship between structure and complexation ability. The ethers with lowest values of O-C-C-O dihedral angle were found to be the most selective towards Li^+ cation, thus the preorganization of the O-C-C-O torsion angle to a best-fit value plays an important role in the complexation ability of Li^+ cation. Moreover, variable-temperature NMR (VT-NMR) experiments for **69** and **71** allowed to calculate rotational barriers using Eyring plot. The barriers were found to be *ca*. 53.5 and 45.6 kJ/mol, respectively. Consequently, these isomeric compounds can adopt a best-fit conformation due to a relatively low energy barrier. In contrast, such a conformational change wasn't observed for ethers **70** and **72**. Presumably, it is not possible to form a 14-membered ring for the diaxial oxygen atoms. The same holds true for *trans*-diadamantyl derivative **73**.

Although reported selectivity factors log($k_{Li,j}$) suggest that certain 14-crown-4 derivatives are promising candidates for lithium extraction, systematic data on Li/Mg, Li/Na, and Li/Ca separation under realistic brine ionic strengths and p*H* conditions remain scarce. Furthermore, the absence of adsorption and extraction isotherms, distribution coefficients, and phase-ratio analyses for these systems limits their practical application. Addressing this knowledge gap is essential for advancing lithium extraction techniques.

Extraction systems and hybrid materials based on 14-crown-4 derivatives

Incorporation of crown ethers in PVC membranes is a convenient method for determination of selectivity coefficients. However, fabrication of extraction devices for preparative separation of lithium may turn out to be less trivial. Preparation of crown ether-based adsorptive separation membrane working in flow regime was recently reported.[18]



14C4PI

Figure 9. Structure of the copolymer **14C4PI**.

A crown ether based copolymer **14C4PI** prepared by condensation polymerization between amino-substituted dibenzo-14-crown-4 ether **55** and diphthalic anhydride derivative was used for preparation of separation membrane. The resultant polyimide with high molecular weight (63 kDa) was employed to fabricate microporous membranes by non-solvent induced phase separation using N,N-dimethylformamide (DMF) as a solvent and water as a coagulation bath (Figure 9). The obtained membranes showed porosity *ca*. 80% and high water permeance. The

maximum Li^+ adsorption capacity was 34.05 mg·g^{-1}. Selective extraction of Li^+ was achieved in the presence of Mg^{2+}, Ca^{2+}, Na^+, K^+ ions. Separation factors ranged from 23.5 (Li^+/Mg^{2+}) to 41.2 (Li^+/Ca^{2+}). In addition, recycling dynamic adsorption experiments demonstrated preservation of the membrane capacity after five adsorption-desorption cycles which indicates possibility of potential application for Li^+ separation. The authors showed superior selectivity of the developed membrane to Li^+ compared to some other membrane devices from literature based on various crown ethers.[38–45]

The same research group published a research article describing electrospun nanofiber membrane prepared from similar polyimide-containing dibenzo-14-crown-4 moiety.[46] The polymer was dissolved in DMF and loaded into syringe for the spinning process. The obtained nanofiber membranes demonstrated three-fold increase of a specific surface area compared to previously studied porous membrane fabricated without electrospinning method and Li^+ adsorption capacity was enhanced up to 40.17 mg·g^{-1}. Recyclability of the membrane was also studied to prove its reusability. Six adsorption-desorption cycles led to a negligible loss of Li^+ adsorption capacity. Interestingly, Li^+/Na^+ and Li^+/K^+ selectivity factors were also slightly improved compared to polymeric membrane fabricated without electrospinning method.

Addition of various amounts of diamino-ether **55** to the 14C4PI/DMF spinning solution allowed to prepare nanofiber membranes DAB-g-14C4PI with even higher Li^+ adsorption capacity up to 60.17 mg·g^{-1}.[47] The authors suggest that a crosslinking process occurs between the polymer and diamino ether. The prepared material retains its nanofiber structure and possesses greater adsorption capacity compared to other polyimide structures described by the authors. The regeneration performance was also decent which is attributed to the amide bond formation between ether **55** and 14C4PI (Figure 10).

Another method of incorporation of dibenzo-14-crown-4 ether in a polymeric membrane was recently utilized for lithium extraction.[45] Radical polymerization of α-methacrylic acid in the presence of dibenzo-14-crown-4 ether afforded material capable of selective lithium extraction from water. The authors showed Li^+ adsorption capacity up to *ca*. 20 mg·g^{-1}. The Li^+ adsorption capacity also revealed p*H*-dependence due to the presence of carboxy-groups in the polymer chains, though the maximum capacity was observed at p*H* 7. It was shown that the hybrid material possesses significantly higher Li^+ capacity compared to corresponding unmodified polymers (polymers prepared without dibenzo-14-crown-4 ether and $LiNO_3$ or without $LiNO_3$). Selectivity factors relative to Na^+, K^+ and Mg^{2+} were found to be 9.2, 10.7 and 3.9, respectively. Moreover, decent recyclability of the hybrid material was shown after 10 adsorption-desorption cycles.

Crown ethers can also be bound to carbon nanotubes as solid supports.[38] A hybrid material can be prepared from multi-walled carbon nanotubes and ether **63** (Figure 11). The authors studied thermal stability of the material and effect of sonication time on the degree of oxidation of MWCNTs surface. Li^+ extraction efficiency was proven to be a p*H*-dependent value for the hybrid material, though MWCNTs-14HBDC4-COOH demonstrated much better extraction efficiency up to 80%. Interestingly, extraction efficiency of MWCNTs-14HBDC4 didn't exceed 20% in all p*H* range. Both materials were more effective in basic solution with p*H* value *ca*. 11, though MWCNT-s-14HBDC4-COOH showed drastic increase of extraction efficiency upon increasing p*H* value. The authors suggest that axial carboxy groups ensure enhanced Li^+ uptake upon deprotonation in basic solutions (substituent **X** in Figure 11). However, the selectivity was not great in the presence of competing ions, *e.g.*, Na^+ and Mg^{2+}, that was discussed above. Introduction of axial carboxy groups may decrease Li^+ selectivity since these side arms may be flexible enough to allow participation in six- to eight-coordination binding of larger cations (Figure 3). The equilibrium adsorption capacity of MWCNTs-14HBDC4-COOH material reached the highest value of 5.4 mg·g^{-1} at initial Li^+ concentration *ca*. 120 mg/L.

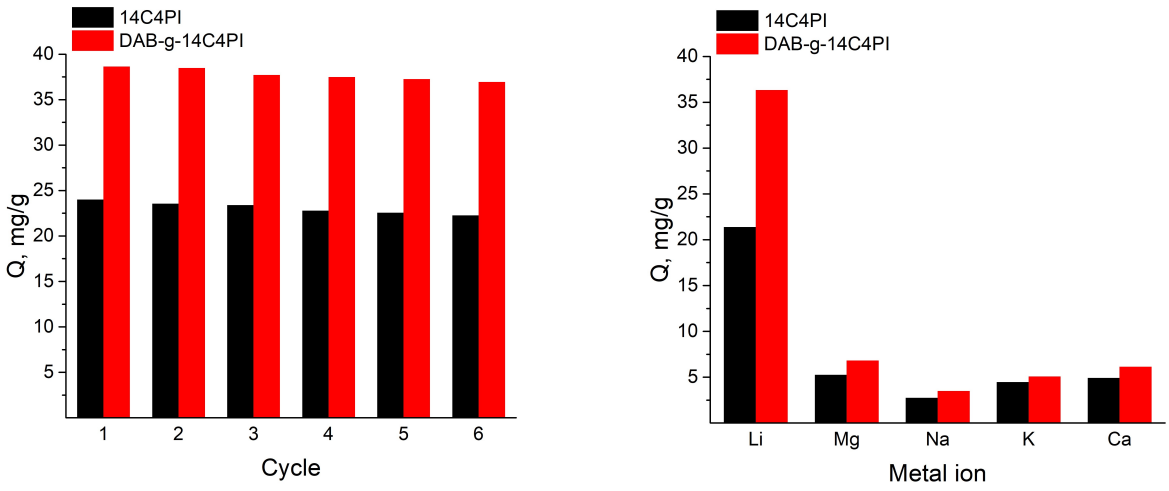


Figure 10. Recyclability of **14C4PI** membrane with or without grafting of diamino ether **55** (left); Selectivity of **14C4PI** membranes with or without grafting of diamino ether **55** (right).

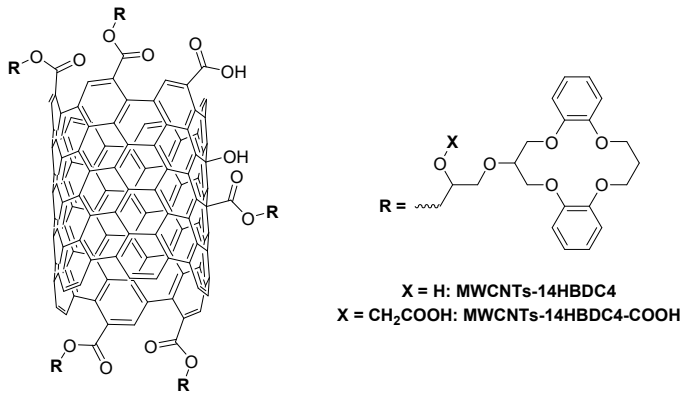


Figure 11. Structure of carbon nanotubes-supported dibenzo-14-crown-4 ether.

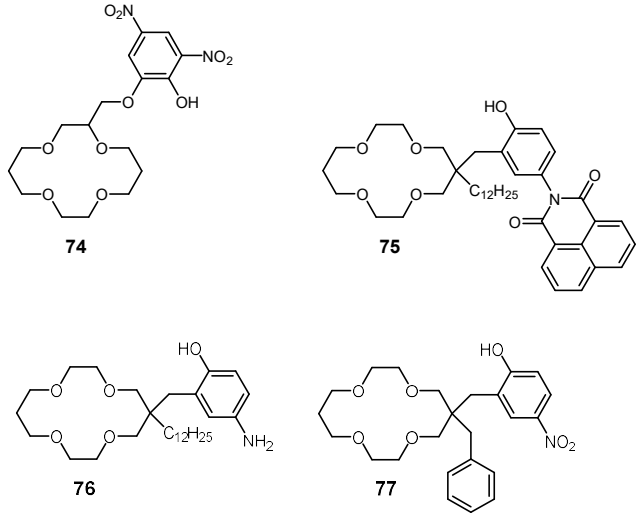


Figure 12. Examples of 14-crown-4 derivatives containing chromophore fragment for UV-Vis detection of lithium in solution.

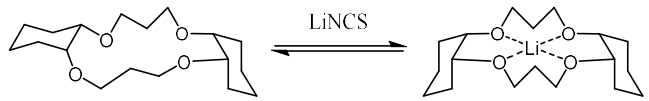


Figure 13. Cyclohexane ring inversion upon complexation of ether **78**.

Covalent immobilization of functionalized 14-crown-4 ether bearing hydroxy-group on crosslinked polymer supports may also serve as a method for the fabrication of lithium extraction devices.[48] Various resins containing 14-crown-4 ether were prepared and their Li^+ adsorption capacity was tested. The complexation ability was significantly affected by the hydrophilicity of a polymer matrix. Poly(glycidyl methacrylate) showed the highest performance among three studied copolymers. However, highest Li^+ adsorption capacity value of these resins did not exceed *ca*. 3.1 $mg \cdot g^{-1}$ which is notably lower than previously discussed results.

Resins containing dibenzo-14-crown-4 ether derivative with carboxy group at C_3 fragment were also prepared by condensation of corresponding ether with formaldehyde in formic acid.[49] In this case Li^+ adsorption capacity also didn't exceed 3.1 $mg \cdot g^{-1}$ for all studied resins and the selectivity in the presence of competing alkali ions was lower compared to more recent results from literature.

Spectrophotometric detection of lithium in solution

There is a number of 14-crown-4 derivatives containing phenol or naphthalenedicarboximido moiety with absorption or luminescence response upon complexation of Li^+ ion (Figure 12).[10,50,51] The complexation process is accompanied by changes in the absorption and fluorescence spectra. As expected, Li^+ ion induced the largest spectral response, while other alkali metals changed the spectra slightly. In addition, pH-dependent behavior of absorption spectra was observed for some crown-ether derivatives. The latter can be used to distinguish between Li^+ and Na^+ ions in aqueous solutions since the influence of p*H* value on the absorption intensity is notably different for these ions. Fluorescence quenching was observed in the presence of lithium cations, which in general can be used for development of fluorescent systems for quantification of Li^+ after calibration.

X-Ray and NMR studies of 14-crown-4 and its derivatives

Conformational analysis of crown ethers is essential for explanation of their complexation properties, in this respect elucidation of crystallographic structures of these ethers and their complexes may provide useful insights into the complexation features. Crystallographic structures of free *syn*-dicyclohexano-14-crown-4 **78** and its LiNCS complex were compared[52] to prove that an inversion of one of the cyclohexane rings occurs upon complexation of lithium isothiocyanate (Figure 13). In the form of a free ether the cyclohexane ring inverts presumably to minimize the electron repulsion between oxygen lone pairs. ^{13}C CPMAS NMR experiment was performed and allowed clear observation of resolved resonances with relative intensities that reflect the mirror plane of symmetry for Li complex of **78**. In contrast, the same experiment for free ether **78** showed the nonequivalence of OCH_2 carbons. These findings are also supported by the X-ray data. Interestingly, the conformational changes of dibenzo-14-crown-4 ether are less drastic compared to some aliphatic 14-crown-4 derivatives,[33] since two benzene rings pre-organize the rigid cavity for Li ion.

Another research of isomeric 14-crown-4 ethers and their LiSCN complexes shows that there is no obvious correlation between preorganization of ether conformation and solvent-extraction selectivity.[53] A number of aliphatic ethers were studied and compared with preorganized dibenzo-14-crown-4 ether. However, some non-preorganized aliphatic ethers demonstrated similar or even better Li^+ selectivity compared to dibenzo-14-crown-4. It allows to conclude that rigidity, preorganization and bulkiness of the ligands provides important yet insufficient information about their complexation abilities.

Crown ether with peripheral oxygen-containing substituents capable of coordination of metal ions were already discussed above.[28,30,31] However, it was found[54] that the crystal structure of dibenzo-14-crown-4-oxyacetate **64** complex with lithium ion contains an apical water molecule, while the pendant arm forms a hydrogen bond with the water molecule (Figure 14). The authors claim that water forms an extensively ordered framework within the studied crystal structure which is dominated by O_5 pentagons. Their attempts to isolate single crystals in water-free solutions were unsuccessful. This peculiarity certainly affects the complexation properties of ether **64**, this molecule is known to possess low selectivity towards Li^+ compared to other metal ions (Figure 3). In general, 14-crown-4 derivatives bearing pendant arms are known to form complexes with Na^+ ion.[55–57] The X-ray structure of **64** with Li^+ ion is in agreement with suggestions that ether **64** possesses too short side arm which can't bring the oxygen atom into a proper apical position for Li^+ coordination. Consequently, the ability of water molecule to occupy an apical position in crown-ether complexes should be accounted while discussing or modeling their extraction properties. The latter statement may be supported with X-ray structure of hydroxydibenzo-14-crown-4 **63**.[30] A water molecule forms 1:1 neutral complex with the crown ether. In this complex, the water molecule is hydrogen bonded by the pendant hydroxyl group of crown ether. A similar arrangement of molecules can be observed in X-ray structures of hydroxy-dibenzo-14-crown-4 ethers bearing two hydroxy-groups.[58] Therefore, interaction with water molecules of crown-ethers containing functional group capable of hydrogen-bonding should be considered for both free ether and its complex with Li ion.

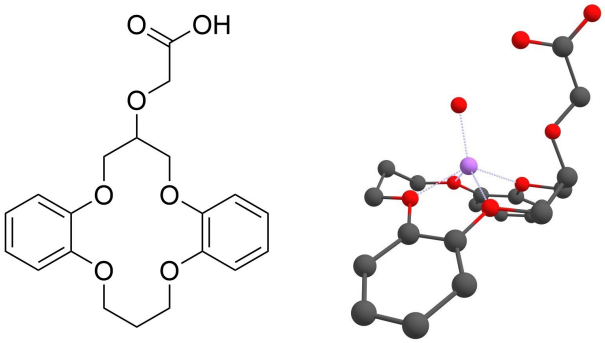


Figure 14. Molecular structure of dibenzo-14-crown-4-oxyacetate **64** (left) and X-ray structure of complex with lithium cation and a water molecule (right). Positional parameters of hydrogen atoms were not listed.

NMR spectroscopy was found to be useful for determination of solution structures of crown ether complexes with alkali metals.[59]. Chemical shift differences for diastereotopic protons provide information about conformational changes upon complexation. Moreover, a determination of sidearm participation in coordination is also possible. Formation constants of crown ether complexes with Li can be determined with ^{7}Li NMR spectroscopy which is of high importance for development of efficient extraction systems.[60,61] The authors found that the nature of a substituent at position 4 in a benzene ring notably affects the formation constant (Figure 15).

Thus, dibenzo-14-crown-4 ethers bearing electron-donating substituents demonstrated higher values of formation constants (from 30 to 50-fold increase). Variation of ^{7}Li chemical shifts as a function of the molar ratio [crown]/[Li^+] in nonaqueous media was also used by the authors to study the complexation process. It was shown that no complexation occurs in DMSO and DMF, weak and medium complexes are formed in THF, pyridine, propylene carbonate and acetone. Strong complexes were formed in acetonitrile and nitromethane.

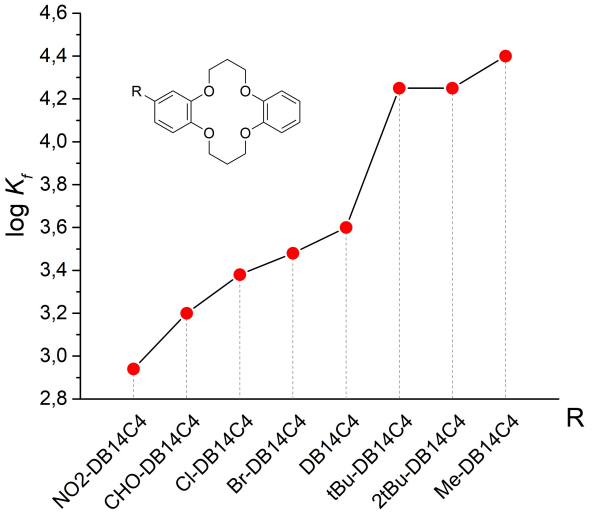


Figure 15. Formation constants of some dibenzo-14-crown-4 ether derivatives with Li determined with ^{7}Li NMR spectroscopy

Comparison of separation factors of 14-crown-4 ethers and their analogues

A review on the extraction properties of 14-crown-4 ethers should also consider their separation factors and corresponding values for other crown ethers for more detailed and informative comparison. For a pair of ions *i*, *j* the separation factor (often denoted as SF*i-j* or α) is defined as a ratio of their distribution coefficients, where a distribution coefficient of ion *i* is the ratio of concentrations of the ion in two immiscible solvents, namely in water and organic solvent. Recent literature reports compare the separation factors rather than selectivity coefficients log $k_{Li,j}$ for various compounds. The approach allows to compare extraction properties of different membraned-based materials and homogeneous liquid-liquid extraction systems.

A comprehensive overview of separation factors for various crown ether–based extractants and membrane materials has recently been reported in the literature.[6,62,63] Some data provided by the authors is shown in Table 1. It can be seen that derivatives of 14-crown-4 ethers exhibit comparable or better Li^+/Na^+, Li^+/K^+ and Li^+/Mg^{2+} selectivities compared to other crown ethers, namely, 18-crown-6, 15-crown-5 and 12-crown-4. In particular, (TBP)-14-crown-4 [C_4mim][NTf_2] extractant demonstrated superior.

Table 1. Comparison of various crown ether-based materials and CE-based liquid-liquid extraction systems.

Material	Crown Ether	Separation factors	Ref.
DB14C4-C16 extractant	DB14C4	Li^+/Na^+: 16.3; Li^+/K^+: 24.5 Li^+/Mg^{2+}: 4.0; Li^+/Ca^{2+}: 68.1	[15]
(TBP)-14-crown-4 [C_4mim][NTf_2] extractant	14C4	Li^+/Mg^{2+}: 515	[62]
PI@14C4 membrane	14C4	Li^+/Mg^{2+}: 14.1	[62]
PEI@DA18C6-PANanofiltration membrane	18C6	Li^+/Mg^{2+}: 11.2	[64]
PEI (15C5)/GO-TMCNanofiltration membrane	15C5	Li^+/Mg^{2+}: 17.5	[65]
PEI@4A-B15C5 Nanofiltration membrane	B15C5	Li^+/Mg^{2+}: 17.4	[66]
2H12C4-D113 resin	12C4	Li^+/Na^+: 2.6; Li^+/K^+: 2.0	[67]
PSf-sg-AB12C4 membrane	12C4	Li^+/Na^+: 33.1; Li^+/Ca^{2+}: 27.1 Li^+/Mg^{2+}: 3.4; Li^+/K^+: 38.4	[68]
TiO2/PVDF/KH550/12CE/TEOS membrane	12C4	Li^+/Mg^{2+}: 6.8; Li^+/K^+: 17.0 Li^+/Ca^{2+}: 21.3; Li^+/Na^+: 24.6	[69]

Li^+/Mg^{2+} separation factor of 515. Membrane PI@14C4 also showed decent Li^+/Mg^{2+} selectivity, proving the applicability of these derivatives for lithium extraction. It should be noted that there are a lot of crown membrane materials with significantly smaller separation factors, thus 14-crown-4 derivatives belong to the higher-performing class of lithium-selective materials.

There is also a research paper where authors report outstandingly high selectivity towards lithium for 14-crown-4 derivatives.[29] It was reported that benzo-14-crown-4 derivatives bearing alkoxy substituents at C_3 fragment possess selectivity coefficients $\alpha_{Li/Na}$, $\alpha_{Li/K}$ and $\alpha_{Li/Cs}$ ranging from 100 to 2500 (liquid-liquid extraction). The obtained results suggest that 14-crown-4 ethers are promising compounds for selective extraction of lithium.

There are a lot of properties besides separation factors which should be considered while discussing different crown ethers, *e.g.* lithium adsorption capacity and reusability of membrane materials, distribution between water and organic phase for liquid-liquid extraction, Mg^{2+} rejection rate, *etc*. Separation factors also may depend on absolute and relative concentrations of both ions in solution, thus they should be compared with care. Finally, synthetic availability of described crown ethers should be kept in mind while discussing their potential application.

Among the 14-crown-4 derivatives discussed in the review, the aliphatic ethers **65**, **66**, **67** and **68** possess exceptional selectivity factors $\log(k_{Li,j})$. Importantly, these compounds contain fewer substituents in the macrocyclic core and therefore can be synthesized in fewer steps compared to highly functionalized molecules as **11** or **58**. As it was mentioned before, selectivity factors alone are not sufficient to guarantee applicability of a given compound in extraction, though the existing data allows to suggest that these ethers are of high interest for further investigation of their extraction properties.

Conclusions

The present review summarizes current knowledge on the synthesis, ion selectivity, and extraction properties of 14-crown-4 ethers. Various synthetic routes towards substituted 14-crown-4 ethers were outlined. Analysis of ion selectivity data demonstrated the significant impact of peripheral substituents on lithium extraction efficiency. In addition, selected hybrid materials incorporating 14-crown-4 units and their performance in extraction processes were reviewed. Lastly, conformational analysis of crown ethers was considered as a powerful tool for gaining insights into the mechanisms of lithium coordination. It is important to note that systematic data on Li/Mg, Li/Na, and Li/Ca separation under realistic brine conditions for 14-crown-4 derivatives remain scarce. This review emphasizes the existing gap and we hope it will assist researchers in advancing the development of next-generation lithium-selective extractants based on the 14-crown-4 scaffold.

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References

1. Gruber P.W., Medina P.A., Keoleian G.A., Kesler S.E., Everson M.P., Wallington T.J. Global lithium availability: A constraint for electric vehicles? *J. Ind. Ecol.* **2011**, *15*, 760–775. https://doi.org/10.1111/j.1530-9290.2011.00359.x.
2. Kesler S.E., Gruber P.W., Medina P.A., Keoleian G.A., Everson M.P., Wallington T.J. Global lithium resources: Relative importance of pegmatite, brine and other deposits. *Ore. Geol. Rev.* **2012**, *48*, 55–69. https://doi.org/10.1016/j.oregeorev.2012.05.006.
3. Vikström H., Davidsson S., Höök M. Lithium availability and future production outlooks. *Appl. Energy* **2013**, *110*, 252–266. https://doi.org/10.1016/j.apenergy.2013.04.005.
4. Yang S., Zhang F., Ding H., He P., Zhou H. Lithium Metal Extraction from Seawater. *Joule* **2018**, *2*, 1648–1651. https://doi.org/10.1016/j.joule.2018.07.006.
5. a) Choubey P.K., Chung K.-S., Kim M., Lee J., Srivastava R.R. Advance review on the exploitation of the prominent energy-storage element Lithium. Part II: From sea water and spent lithium ion batteries (LIBs). *Miner. Eng.* **2017**, *110*, 104–121. https://doi.org/10.1016/j.mineng.2017.04.008; b) Vikulova M.A., Maximova L.A., Rudyh V.Y., Gorokhovsky A.V. Li^+ Extraction from aqueous solutions by PVDF-based membranes containing partially protonated potassium polytitanate. *ChemChemTech* **2024**, *67*(5), 62–69. https://doi.org/10.6060/ivkkt.20246705.6969

6. Yin X., Xu P., Wang H. Applications of crown ether-based materials for enhancing lithium recovery from brines. *Sep. Purif. Technol.* **2025**, *371*, 133093. https://doi.org/10.1016/j.seppur.2025.133093.
7. Kimura K., Yano H., Kitazawa S., Shono T. Synthesis and selectivity for lithium of lipophilic 14-crown-4 derivatives bearing bulky substituents or an additional binding site in the side arm. *J. Chem. Soc. Perkin Trans. 2* **1986**, *4*, 1945–1951. https://doi.org/10.1039/P29860001945.
8. Kimura K., Tanaka M., Iketani S., Shono T. Synthesis and cation-extraction study of lithium-selective chromogenic 14-crown-4 derivatives. *J. Org. Chem.* **1987**, *52*, 836–844. https://doi.org/10.1021/jo00381a023.
9. Kitazawa S., Kimura K., Yano H., Shono T. Lipophilic Crown-4 Derivatives as Lithium Ionophores. *J. Am. Chem. Soc.* **1984**, *106*, 6978–6983. https://doi.org/10.1021/ja00335a019.
10. Shibutani Y., Sakamoto H., Hayano K., Shono T. Synthesis and cation-extraction study of chromogenic 14-crown-4 derivatives for spectrophotometric determination of lithium. *Anal. Chim. Acta* **1998**, *375*, 81–88. https://doi.org/10.1016/S0003-2670(98)00263-3.
11. Tobe Y., Tsuchiya Y., Iketani H., Naemura K., Kobiro K., Kaji M., et al. Synthesis and lithium ion selectivity of 14-crown-4 derivatives having bulky subunits: cis and trans isomers of 2-phenylcyclohexano-14-crown-4, 2,3-diphenylcyclohexano-14-crown-4 and 2,3-di-(1-adamantyl)-14-crown-4. *J. Chem. Soc. - Perkin. Trans. 1* **1998**, *4*, 485–494. https://doi.org/10.1039/a706606f.
12. Sachleben R.A., Davis M.C., Bruce J.J., Ripple E.S., Driver J.L., Moyer B.A. An efficient synthesis of lithium-selective extractants: Tertiary-alkyl-14-crown-4 ethers. *Tetrahedron Lett.* **1993**, *34*, 5373–53766. https://doi.org/10.1016/S0040-4039(00)73912-8.
13. Czech B.P., Zazulak W., Kumar A., Olsher U., Feinberg H., Cohen S., et al. Synthesis of substituted 14-crown-4 compounds. *J. Heterocycl. Chem*. **1992**, *29*, 1389–400. https://doi.org/10.1002/jhet.5570290604.
14. Chen C.S., Wang S.J., Wu S.C. A template effect in the synthesis of dibenzo-14-crown-4 derivatives. *J. Heterocycl. Chem.* **1983**, *20*, 795–798. https://doi.org/10.1002/jhet.5570200358.
15. Xiong Y., Ge T., Xu L., Wang L., He J., Zhou X., et al. A fundamental study on selective extraction of Li^+ with dibenzo-14-crown-4 ether: Toward new technology development for lithium recovery from brines. *J. Environ. Manage* **2022**, *310*, 114705. https://doi.org/10.1016/ j.jenvman.2022.114705.
16. Chen W., Tian Y., Hu C., Zhao Z., Xu L., Tong B. Theoretical and extraction studies on the selectivity of lithium with 14C4 derivatives. *New J. Chem.* **2020**, *44*, 20341–20350. https://doi.org/10.1039/d0nj04404k.
17. Kuan T.C., Chiou C.L., Wang S.J. Facile syntheses of dibenzo-14-crown-41a and bis-butylbenzo-14-crown-4. *Synth. Commun.* **1982**, *12*, 477–483. https://doi.org/10.1080/00397918208065955.
18. Zhu Q., Ma X., Pei H., Li J.J., Yan F., Cui Z., et al. A highly-efficient lithium adsorptive separation membrane derived from a polyimide-containing dibenzo-14-crown-4 moiety. *Sep. Purif. Technol.* **2020**, *247*, 116940. https://doi.org/10.1016/j.seppur.2020.116940.
19. Torrejos R.E.C., Nisola G.M., Song H.S., Han J.W., Lawagon C.P., Seo J.G., et al. Liquid-liquid extraction of lithium using lipophilic dibenzo-14-crown-4 ether carboxylic acid in hydrophobic room temperature ionic liquid. *Hydrometallurgy* **2016**, *164*, 362–371. https://doi.org/10.1016/j.hydromet.2016.05.010.
20. Bakker E., Meyerhoff M.E. Ionophore-based membrane electrodes: New analytical concepts and non-classical response mechanisms. *Anal. Chim. Acta* **2000**, *416*, 121–137. https://doi.org/10.1016/S0003-2670(00)00883-7.
21. Bakker E., Bühlmann P., Pretsch E. Polymer membrane ion-selective electrodes-what are the limits? *Electroanalysis* **1999**, *11*, 915–933. https://doi.org/10.1002/(SICI)1521-4109(199909)11:13<915::AID-ELAN915>3.0.CO;2-J.
22. Pechenkina I.A., Mikhelson K.N. Materials for the ionophore-based membranes for ion-selective electrodes: Problems and achievements (review paper). *Russ. J. Electrochem.* **2015**, *51*, 93–102. https://doi.org/10.1134/S1023193515020111.
23. Eisenman G., Rudin D.O., Casby J.U. Glass Electrode for Measuring Sodium Ion. *Science* **1957**, *126*, 831–834. https://doi.org/10.1126/science.126.3278.831.
24. Suzuki K., Tohda K., Aruga H., Matsuzoe M., Inoue H., Shirai T. Ion-Selective Electrodes Based on Natural Carboxylic Polyether Antibiotics. *Anal. Chem.* **1988**, *60*, 1714–1721. https://doi.org/10.1021/ac00168a016.
25. Kitazawa S., Kimura K., Yano H., Shono T. Lithium-selective polymeric membrane electrodes based on dodecylmethyl-14-crown-4. *Analyst* **1985**, *110*, 295–299. https://doi.org/10.1039/an9851000295.
26. Olsher U. The Lipophilic Macrocyclic Polyether 2,3,9,10-Dibenzo-1,4,8,1 l-tetraoxacyclotetradeca- 2,9-diene (Dibenzo- 14-crown-4): A Selective Ionophore for Lithium Ions. J. Am. Chem. Soc 1982, 104, 4006–4007. https://doi.org/10.1021/ ja01848a068.
27. Suzuki K., Yamada H., Sato K., Watanabe K, Hisamoto H, Tobe Y, et al. Design and Synthesis of Highly Selective Ionophores for Lithium Ion Based on 14-crown-4 Derivatives for an Ion-Selective Electrode. *Anal. Chem.* **1993**, *65*, 3404–3410. https://doi.org/10.1021/ac00071a012.
28. Olsher U., Frolow F., Shoham G., Heo G.S., Bartsch R.A. Alkali-Metal and Alkaline-Earth Cation and Proton Selectivities of Dibenzo-14-crown-4 and Its Derivatives in Polymeric Membranes. *Anal. Chem*. **1989**, *61*, 1618–1621. https://doi.org/10.1021/ac00190a006.
29. Torrejos R.E.C., Nisola G.M., Song H.S., Limjuco L.A., Lawagon C.P., Parohinog K.J., et al. Design of lithium selective crown ethers: Synthesis, extraction and theoretical binding studies. *Chem. Eng. J.* **2017**, *326*, 921–933. https://doi.org/10.1016/j.cej.2017.06.005.
30. Olsher U., Frolow F., Bartsch R.A., Pugia M.J., Shoham G. Crown ether alcohols. 1. Crystal and molecular structure of the complex between sym-hydroxydibenzo-14-crown-4 and water molecules ([C18H20O5].cntdot.1.25[H2O].cntdot.0.125[CH3OH]) including interesting water-methanol channels. *J. Am. Chem. Soc.* **1989**, *111*, 9217–9222. https://doi.org/10.1021/ja00208a015.
31. Shoham G., Lipscomb W.N., Olsher U. X-Ray crystal and molecular structure of the complex between dibenzo-14-crown-4 and LiSCN. *J. Chem. Soc. Chem. Commun.* **1983**, 208. https://doi.org/10.1039/c39830000208.
32. Holt E.M., Malpass Jnr G.D., Ghirardelli R.G., Palmer R.A., Rubin B. Crown-ether complexes. IV. Lithium nitrate complex with benzo-14-crown-4, LiNO3.C14H20O4. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **1984**, *40*, 394–396. https://doi.org/10.1107/s0108270184004261.
33. Sachleben R.A., Burns J.H. Conformational changes of substituted 14-crown-4 ethers upon complexation. *J. Chem. Soc. Perkin Trans. 2* **1992**, 1971–1977. https://doi.org/10.1039/p29920001971.
34. Kimura K., Maeda T., Tamura H., Shono T. Potassium-selective PVC membrane electrodes based on bis- and poly(crown ether)s. *J. Electroanal. Chem.* **1979**, *95*, 91–101. https://doi.org/10.1016/S0022-0728(79)80222-3.
35. Kimura K., Tamura H., Shono T. Caesium-selective PVC membrane electrodes based on bis(crown ether)s. *J. Electroanal. Chem.* **1979**, *105*, 335–340. https://doi.org/10.1016/S0022-0728(79)80127-8.
36. Kimura K., Tamura H., Shono T. A highly selective ionophore for potassium ions: A lipophilic bis(15-crown-5)

derivative. *J. Chem. Soc. Chem. Commun.* **1983**, 492–493. https://doi.org/10.1039/c39830000492.
37. Kobiro K., Tobe Y., Watanabe K., Yamada H., Suzuki K. Highly Selective Lithium Ion Electrode Based on Decalino-14-Crown-4. *Anal. Lett.* **1993**, *26*, 49–54. https://doi.org/10.1080/00032719308016794.
38. Torrejos R.E.C., Nisola G.M., Park M.J., Shon H.K., Seo J.G., Koo S., et al. Synthesis and characterization of multi-walled carbon nanotubes-supported dibenzo-14-crown-4 ether with proton ionizable carboxyl sidearm as Li^+ adsorbents. *Chem. Eng. J.* **2015**, *264*, 89–98. https://doi.org/10.1016/j.cej.2014.11.036.
39. Sun D., Zhu Y., Meng M., Qiao Y., Yan Y., Li C. Fabrication of highly selective ion imprinted macroporous membranes with crown ether for targeted separation of lithium ion. *Sep. Purif. Technol.* **2017**, *175*, 19–26. https://doi.org/10.1016/j.seppur.2016.11.029.
40. Luo X., Zhong W., Luo J., Yang L., Long J., Guo B., et al. Lithium ion-imprinted polymers with hydrophilic PHEMA polymer brushes: The role of grafting density in anti-interference and anti-blockage in wastewater. *J. Colloid Interface Sci.* **2017**, *492*, 146–156. https://doi.org/10.1016/j.jcis.2016.12.065.
41. Yan F., Liu Y., Wang M., Yang B., Pei H., Li J., et al. Preparation of polysulfone-graft-monoazabenzo-15-crown-5 ether porous membrane for lithium isotope separation. *J. Radioanal. Nucl. Chem.* **2018**, *317*, 111–119. https://doi.org/10.1007/s10967-018-5918-x.
42. Liu Y., Yan F., Pei H., Li J., Cui Z., He B., et al. Preparation of PSf-g-BN15C5/NWF composite membrane with sponge-like pore structure for lithium isotopes adsorptive separation. *J. Taiwan Inst. Chem. Eng.* **2018**, *91*, 507–516. https://doi.org/10.1016/j.jtice.2018.05.031.
43. Pei H., Yan F., Ma X., Li X., Liu C., Li J., et al. In situ one-pot formation of crown ether functionalized polysulfone membranes for highly efficient lithium isotope adsorptive separation. *Eur. Polym. J.* **2018**, *109*, 288–296. https://doi.org/10.1016/j.eurpolymj.2018.10.001.
44. Wang W., Julaiti P., Ye G., Huo X., Chen J. Controlled architecture of macrocyclic ligand functionalized polymer brushes from glass fibers using surface-initiated ICAR ATRP technique for adsorptive separation of lithium isotopes. *Chem. Eng. J.* **2018**, *336*, 669–78. https://doi.org/10.1016/j.cej.2017.12.045.
45. Huang Y., Wang R. Highly Effective and Low-Cost Ion-Imprinted Polymers Loaded on Pretreated Vermiculite for Lithium Recovery. *Ind. Eng. Chem. Res.* **2019**, *58*, 12216–12225. https://doi.org/10.1021/acs.iecr.9b01244.
46. Yang F., Li L., Hua J., He J., Ma X., Li J. Electrospun nanofiber membrane of dibenzo 14-crown-4-ether polyimide for efficient selective lithium recovery from discarded lithium-ion batteries. *Sep. Purif. Technol.* **2024**, *334*, 126018. https://doi.org/10.1016/j.seppur.2023.126018.
47. Yang F., Hua J., Du J., He J., Xiao J., Li L., et al. Electrospun nanofiber membrane of 14-crown-4 polyimide by in situ grafting diamino crown ether for highly selective Li^+ adsorption and separation. *Sep. Purif. Technol.* **2024**, *351*, 128097. https://doi.org/10.1016/j.seppur.2024.128097.
48. Alexandratos S.D., Stine C.L., Sachleben R.A., Moyer B.A. Immobilization of lithium-selective 14-crown-4 on cross-linked polymer supports. *Polymer (Guildf)* **2005**, *46*, 6347–6352. https://doi.org/10.1016/j.polymer.2004.10.091.
49. Hayashita T., Lee J.H., Hankins M.G., Lee J.C., Kim J.S., Knobeloch J.M., et al. Selective Sorption and Column Concentration of Alkali-Metal Cations by Carboxylic Acid Resins with Dibenzo-14-Crown-4 Subunits and their Acyclic Polyether Analogues. *Anal. Chem.* **1992**, *64*, 815–819. https://doi.org/10.1021/ac00031a021.
50. Kimura K., Iketani S., Shono T. Synthesis of a fluorescent 14-crown-4 derivative bearing a proton-dissociable moiety and its use for selective lithium-ion extraction. *Anal. Chim. Acta* **1987**, *203*, 85–89. https://doi.org/10.1016/0003-2670(87)90010-9.
51. Kimura K., Iketani S.I., Sakamoto H., Shono T. Flow injection of lithium ion using chromogenic 14-crown-4 derivatives as extraction-spectrophotometric reagents. *Analyst* **1990**, *115*, 1251–1255. https://doi.org/10.1039/AN9901501251.
52. Buchanan G.W., Kirby R.A., Charland J.P. Stereochemistry of crown ethers and their complexes in the solid state. Carbon-13 CPMAS NMR and x-ray crystallographic studies of configurationally isomeric dicyclohexano-14-crown-4 ethers, dibenzo-14-crown-4 ether, and some lithium thiocyanate salts. *J. Am. Chem. Soc.* **1988**, *110*, 2477–2483. https://doi.org/10.1021/ja00216a022.
53. Burns J.H., Sachleben R.A., Davis M.C. Structures of isomeric substituted 14-crown-4 ethers and their LiSCN complexes. *Inorg. Chim. Acta* **1994**, *223*, 125–130. https://doi.org/10.1016/0020-1693(94)04006-0.
54. Shoham G., Christianson D.W., Bartsch R.A., Heo G.S., Olsher U., Lipscomb W.N. Crystal and Molecular Structure of the Complex between sym-Dibenzo-14-crown-4-oxyacetate and Li^+. *J. Am. Chem. Soc.* **1984**, *106*, 1280–1285. https://doi.org/10.1021/ja00317a018.
55. Burns J.H., Sachleben R.A. Synthesis and Structural Studies of Sodium Complexes of sym-Dibenzo-14-crown-4 Ionizable Lariat Ethers. *Inorg. Chem.* **1990**, *29*, 788–795. https://doi.org/10.1021/ic00329a043.
56. Bryan J.C., Sachleben R.A. Synthesis of a new dibenzo-14-crown-4 lariat ether and structure of its sodium perrhenate complex. *J. Chem. Crystallogr.* **1999**, *29*, 1255–1259. https://doi.org/10.1023/A:1009552806586.
57. Sachleben R.A., Burns J.H., Brown G.M. Synthesis of a Lariat Ether Having a Phosphinic Acid Functional Group and the Crystal Structure of Its Na+ Complex: Sodium sym-[(Dibenzo-14-crown-4-oxy)methyl]phenylphosphinate Dihydrate Diethanolate. *Inorg. Chem.* **1988**, *27*, 1787–1790. https://doi.org/10.1021/ic00283a023.
58. Dalley N.K., Weiming J., Olsher U., Frolow F., Pugia M.J., Yu Z.Y., et al. Crystal structures of dibenzo-14-crown-4 alcohol and diol monohydrates. *J. Incl. Phenom. Mol. Recognit. Chem.* **1995**, *23*, 85–98. https://doi.org/10.1007/BF00707887.
59. Talanov V.S., Purkiss D.W., Bartsch R.A. Solution structures of alkali metal sym-(R)dibenzo-14-crown-4-oxyacetates. *J. Chem. Soc. Perkin. Trans. 2* **2000**, *7*, 749–755. https://doi.org/10.1039/a908474f.
60. Chen C.-S., Tsai Z.-T., Wang S.-J., Chung C.-S. Thermodynamics of Complexation Reactions of Lithium Ion with Dibenzo-14-Crown-4 and Its Analogs in Nonaqueous Solvents. *J. Chinese Chem. Soc.* **1993**, *40*, 255–261. https://doi.org/10.1002/jccs.199300039.
61. Chen C.S., Wang S.J., Wu S.C. Solvent effects in the complexation of dibenzo-14-crown-4 and its analogues with lithium ion. *Inorg. Chem.* **1984**, *23*, 3901–3903. https://doi.org/10.1021/ic00192a013.
62. Hua J., He J., Pei H., Ma X., Wickramasinghe S.R., Li J. Supported ionic liquid membrane contactor with crown ether functionalized polyimide membrane for high-efficient Li^+/Mg^{2+} selective separation. *J. Memb. Sci.* **2023**, 687. https://doi.org/10.1016/j.memsci.2023.122038.
63. Mao L., Chen R., He J., Pei H., He B., Ma X., et al. Remarkably High Li+Adsorptive Separation Polyamide Membrane by Improving the Crown Ether Concentration and Electron Density. *ACS Sustain. Chem. Eng.* **2022**, *10*, 10047–10056. https://doi.org/10.1021/acssuschemeng.2c02950.
64. Zha Z., Li T., Hussein I., Wang Y., Zhao S. Aza-crown ether-coupled polyamide nanofiltration membrane for efficient Li^+/Mg^{2+} separation. *J. Memb. Sci.* **2024**, *695*, 122484. https://doi.org/10.1016/j.memsci.2024.122484.

65. Zheng L., Song X., Liu J., Jiang H., Toghan A. Crown ether regulated nanocomposite membrane with lithium channels for highly selective Li^+/Mg^{2+} separation. *Desalination* **2024**, *592*, 118121. https://doi.org/10.1016/j.desal.2024.118121.
66. He Y., Li G., Lin H., Han Q., Ye Y., Wang J., et al. Enhanced Mg^{2+}/Li^+ separation by amino crown ether composite nanofiltration membrane with Mg^{2+} transport barrier. *J. Memb. Sci.* **2024**, *709*, 123137. https://doi.org/10.1016/j.memsci.2024.123137.
67. Wu Y.H., Guo W., Sun Y.Z., Sun S.Y. Resin functionalized with 2-(hydroxymethyl)-12-crown-4 ether for selective adsorption of lithium ions from desilication solution of coal-based solid waste. *Sep. Purif. Technol.* **2025**, *355*, 129500. https://doi.org/10.1016/j.seppur.2024.129500.
68. Zheng X., Li A., Hua J., Zhang Y., Li Z. Crown ether grafted graphene oxide/chitosan/polyvinyl alcohol nanofiber membrane for highly selective adsorption and separation of lithium ion. *Nanomaterials* **2021**, 11. https://doi.org/10.3390/nano11102668.
69. Yang J., Qu G., Liu C., Zhou S., Li B., Wei Y. An effective lithium ion-imprinted membrane containing 12-crown ether-4 for selective recovery of lithium. *Chem. Eng. Res. Des.* **2022**, *184*, 639–650. https://doi.org/10.1016/j.cherd.2022.06.039.

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