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著者	Rahman Ismail M. M., Begum Zinnat A., Hasegawa Hiroshi
journal or publication title	Microchemical Journal
number	110
page range	485-493
year	2013-09-01
URL	<a href="http://hdl.handle.net/2297/35205">http://hdl.handle.net/2297/35205</a>

doi: 10.1016/j.microc.2013.06.006

The research article is originally published at *Microchemical Journal*  
An Elsevier Journal

<http://www.journals.elsevier.com/microchemical-journal/>

The original publication is available at: <http://dx.doi.org/10.1016/j.microc.2013.06.006>

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## **Selective separation of elements from complex solution matrix with molecular recognition plus macrocycles attached to a solid-phase: A review**

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**Please Cite the article as:** I.M.M. Rahman, Z.A. Begum and H. Hasegawa, Selective separation of elements from complex solution matrix with molecular recognition plus macrocycles attached to a solid-phase: A review, *Microchemical Journal*, 110: 485–493, 2013.

## **Abstract**

Solid-phase extraction (SPE) approach was introduced approximately five decades ago, and until then development of SPE materials is seamlessly continued. Lately, the SPE-based research is increasingly focused in developing more explicit materials to achieve meticulous separation of elements from complex solution matrices with high concentrations of interfering ions. One group of SPE materials includes those with macrocyclic ligands immobilized on a solid-phase, which are capable of selective separation and pre-concentration of elements, and such selectivity in metal retention is generally termed as molecular recognition. In the process, the designed ‘host’ material possesses a high degree of recognition to specific elements or groups of elements called ‘guest’, and the recognition capability remains effective at the very low concentrations of the ‘guest’ species or when those present in complex matrices. The routes to the development of element-selective SPEs, the operating principles, applications and limitations are discussed in this review.

## **Keywords**

Separation; element-selectivity; Macrocycles; Solid-phase extraction; Molecular recognition

## **1.0 Introduction**

Although metals and metalloids are ubiquitous in nature, the environmental concentrations of both toxic and essential elements have been largely increased mostly pursuant to anthropogenic activities related to the industrial development and improved living standards in modern societies. The growing extent of metal pollution also initiated a number of legislative measures, such as, the Restriction of Hazardous Substance (RoHS) directive [1], End of Life Vehicle (ELV) directive [2] or the European Union Council Directive [3]. The RoHS or ELV directive has been imposed to specify the limit of trace elements in the industrial products, while the EU directive defined the acceptable concentrations of different elements in cultivable soils.

Sensitive analytical techniques such as, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry, and so forth are available for precise analysis of trace elements in solution. An overall analytical process comprises a number of succeeding steps, including sampling, sample preparation, separation and quantification. Among the aforementioned steps, sample preparation is by far the most important error source in modern analytical method development due to the low species concentration or heterogeneous distribution of the analytes in the matrix as well as the complex nature of the sample matrices. Therefore, a clean-up/separation step is often recommended before the analytical determination of trace elements in effluent or industrial waste waters to avoid the interfering effect from the matrix ions or to facilitate preconcentration due to their low concentrations in samples. The techniques commonly used for separation of elements from the matrix components are co-precipitation [4, 5], solvent extraction or liquid-liquid extraction [6], cloud point extraction [7-10], membrane filtration

[11-14], and solid-phase extraction (SPE) [15]. Most of the conventional separation approaches undergo slow kinetics and, also, lose effectiveness when the concentration of the species to be separated is low, or when several other chemically-similar elements to the target species co-exist in the matrix. The SPE-approach coupled with macrocycles of molecular recognition capability was introduced as an effectual separation system, which possess sufficient specificity and superior affinity for the target element or group of elements over other closely related elements, even if these elements are present in high concentration. The review covers the background of the development of the SPE-systems with macrocycles, including the operating routes. The whys and wherefores of the selectivity behavior have been explained, and the application examples are compiled including the limitations in developments.

## **2.0 Development of SPE materials: activated carbon to macrocycles**

In SPE, analyte(s) is isolated from a solution by their transfer to and retention on a solid-phase sorbent packed in any of the following formats: micro-columns, cartridges, syringe barrels and disks. Regardless of the format used, SPE operation involves two major steps— sample loading and elution. Sample solution containing the analytes is allowed to percolate through the solid sorbent material for collection of the analytes in the sample loading step while the ‘captured’ analytes are back-extracted upon elution with a suitable solvent in the final step. A ‘conditioning’ step is always performed before the sample loading step to ensure the removal of any likely impurities contained in the sorbent or the packaging of the SPE system. It also allows the wetting of the packing material and the solvation of the SPE material. An optional washing step using a solvent having low elution strength is sometimes involved between the sample treatment and elution step to eliminate the unwanted matrix components without displacing the target analytes. The flow rates of the sample

loading and elution steps are required to be optimized to attain the quantitative separation performance [16-18]. The progress and developments in solid phase extraction (SPE) technique over the decades were discussed in a number of review articles [15, 18, 19], book sections [16, 17] and books [20-22]. Therefore, a detailed discussion on every single SPE-type is not included in this review. Instead, a timeline-based approach has been used to highlight the property-based development of SPE materials.

The first experimental application of SPE started approximately five decades ago with the application of granular activated carbon for the concentration of organic compounds from raw and filtered surface waters [15, 23]. An attempt to find the more suitable SPE material was started in the late 1960s to overcome the limiting factors of activated carbon due to its heterogeneous nature [15]. Riley and Taylor [24] introduced a cross-linked polystyrene resin, Amberlite XAD-1 for SPE separation of organic compounds from aqueous samples. The study stimulated the interest about Amberlite polymeric resins among other researchers in the 1970s. Consequently, other styrene-divinylbenzene Amberlites (XAD-2, XAD-4) and ethylene-dimethacrylate resins (XAD-7 and XAD-8) were introduced [25-32]. Other copolymers such as, Porapaks [33-35], Chromosorbs [36-41] and Tenax (2,6-diphenyl-p-phenylene oxide) [42-45] were also used for SPE procedures along with Amberlites. The search for the most appropriate SPE material includes the application of polyurethanes either as open-pore polyurethane [46, 47] or as polyurethane foam [48-57], polypropylene [58-60], polytetrafluoroethylene [61-64] or ion-exchange resins [65-68] etc.

There are too many aspects of the resin standardization that had to be considered prior to the analytical use of macroreticular resins, which initiated the evaluation of other types of SPE materials [15]. Applicability of bonded phases for SPE process was introduced in the middle of 1970s [15, 69]. Later, well standardized and relatively stable commercial SPE products with bonded silica became available, which resulted in the extensive use of these

materials in SPE procedures [15]. Although SPE procedures with different alkyl- or aryl-groups bonded with silica were reported, octadecyl-bonded silica is the most popular phase among the bonded phase employing silica's [15, 70-76].

During the search for the best SPE material, it became apparent that there was no universal material suitable for all purposes. It was observed that some of the SPE materials have the capability to interact with a variety of metal ions, while others are fairly specific for a particular ion [77-82]. Lately, there has been increasing interest in developing more explicit materials to use in the meticulous separation of ions from solutions containing complex matrices with high concentrations of interfering ions. Simultaneously, efforts to design more effective SPE systems besides the development of classical types of SPE materials were continued. Membrane extraction disks consisting of a fibrillated PTFE matrix enmeshed with bonded silica, polymers or ion exchangers were designed to achieve higher sample flow rate and selectivity in the separation process [83-85]. Selective affinity of SPE materials towards target substances can also be achieved with the use of molecularly imprinted polymers (MIPs). In MIPs, a chosen target molecule is used as a template through a casting procedure which is extracted afterwards, thus leaving complementary cavities behind. In the process, MIPs show a certain chemical affinity for the original molecule and were successfully used for selective extraction [86, 87]. Solid phase microextraction (SPME) is another new interesting SPE technique, which involves the use of a fiber coated with an extracting phase, that can be a liquid (polymer) or a solid (sorbent), which extracts different kinds of analytes from liquid or gas phase [88-91].

The efforts done in aiming for an optimum material for a particular application with the classical-type SPE application are also not stopped. Analyte-antibody interactions were used to design immunosorbent, which can be used as a classical SPE material. In this approach antibody produced against a target compound is immobilized on a solid phase to achieve

selective extraction [92-97]. One group of classical-type SPE system includes the use of macrocyclic chelants, such as crown ethers, immobilized on a silica or polymer support which was designed to attain selectivity in the separation process [98-107].

A timeline view of the development in SPE materials until the introduction of macrocycle-containing SPEs is illustrated in [Figure 1](#).

### **3.0 Operating route of macrocycles in metal separation**

Macrocyclic compounds have a considerable potential to be used as metal-selective reagents in the separation science due to their ability to form stable complexes with metal ions [108-110]. An enormous number of macrocyclic reagents with a variety of donor atoms, ring sizes, and ligand geometries have been prepared [111]. The foremost group of macrocyclic compounds is crown ethers, and the first crown ether was dibenzo-18-crown-6 [112]. In addition to the crown ethers, other kinds of macrocyclic ligands, e.g., macrocyclic polyamines, polysulphides, cyclic peptides, calixarenes, cyclophanes, and cyclodextrins are available as parent macro-rings [113-115]. A comparison of the parent macrocycles characteristics is summarized in [Table 1](#). Among the parent macrocycles, crown ethers possess excellent structural diversity followed by superior guest selectivity, and are particularly effective for binding hard metal ions [113].

Crown ethers contain oxygen, sulfur and nitrogen as donor atoms. The number of donor atoms in the crown ether unit determines the stability of the macrocycle-metal complex while the types of donor atoms decide the ion selectivity of the crown ethers [116]. The metal ion binding strength and selectivity can be strengthened by the introduction of one or more side arms into the crown ether unit, and the derivative is known as lariat ether [113, 117, 118]. Complexes containing species incorporated in the macrocyclic cavity are known as inclusion complexes, and different types of complexation between the macrocycle structure and the



target metal ions are likely [115]. Some possible types of complexation between  $K^+$  with diaza-18-crown-6, lariat ether and double armed crown ether as reported by Gandour et al. [119] and reproduced by Tsukube [113] are shown in Fig. 2a. Figure 2b shows the schematic illustration of the cation binding process with the armed macrocycles [113]. As shown in Fig. 2a, accommodation of  $K^+$  ion in a circular cavity of the parent macrocycle diaza-18-crown-6 **1** is observed. The  $K^+$  ion is coordinated to donor atoms of both crown ring and sidearm in the complex of lariat ether **2**, while it is completely accommodated in a three-dimensional cavity in the double armed crown ether **3** complex [113, 119]. Frequent use of the varying numbers of the sidearms by the armed macrocycles to bind the cations is observed as illustrated in Fig. 2b [113]. Hence, it can be briefly concluded that the selective separation of elements by macrocycles is managed either by the accommodation of ions within their circular cavity or in the three-dimensional cavity-like structures formed between the macro-ring and the sidearms. It also provides the advantage of designing a single macrocycle structure with a diverse selectivity option for target elements of distinctive ionic characters [120, 121] or a multiple-site receptor for different target species [122] as shown in Fig. 3.

Macrocycles have been employed for selective separation of metal ions from mixtures in bulk liquid membrane and/ or solvent extraction systems [116, 123, 124]. However, separation of metal ions using extraction or membrane systems is not considered as a cost-effective option due to the gradual loss of the expensive macrocyclic compounds from the organic membrane or layer [125]. The shortcoming was minimized by attaching the macrocyclic compounds to silica gel using a stable hydrocarbon-ether linkage [99, 100, 106, 125]. The efficiency of such systems lead to the development of new separation systems with the use of solid supported macrocycles, which are capable of high selectivity or recognition towards a particular species of metal or metalloid [104, 125].

#### 4.0 Selective solid-phase extraction of elements using macrocycle-aided molecular recognition

The process of recognition-based SPEs features steps of designing materials with pre-determined species-selectivity, attaching these to the supports, and their use to accomplish the required chemical separations. The designed ‘host’ materials, mostly containing macrocycles, possess a high degree of recognition to specific element or groups of elements called ‘guest’, and the recognition capability remains effective at the very low concentrations of the ‘guest’ species or when those present in complex matrices [104]. Synthesis of such materials includes a combined approach of organic synthesis and the study of cation complexation properties of the crown ethers to design and prepare macrocyclic ligands that will possess selective affinity to the target ions [102, 126, 127]. A compilation of schemes for synthesis of several crown ether varieties *e.g.* thiacrown ethers, diestercrown ethers, proton-ionizable crown ethers, chiral crown ethers, azacrown ethers and so forth is available [127]. As an example, ion-selective behavior of two 5-chloro-8-hydroxyquinoline (CHQ) substituted azacrown ethers (**1** and **2** in Fig. 4) is discussed as described by Zhang et al. [128] and Bordunov et al. [129]. In the azacrown ether structure **1**, two CHQ groups are attached to the macro ring through their positions 7 and exhibit selectivity to  $Mg^{2+}$  ion over other alkali and alkaline earth metal ions. The stronger affinity of **1** to  $Mg^{2+}$  ion maybe due to the incomplete interaction of the OH and quinoline nitrogen atoms in the CHQ groups with a cation bound within the macro ring. The quinoline nitrogens are sterically prevented from approaching the macro ring by the OH groups. Hence, the CHQ groups remain in the proper positions to selectively interact with  $Mg^{2+}$  and the macro ring. The CHQ groups, that are attached through their positions 2, in the macrocycle structure **2** exhibit better selectivity for  $K^+$  and  $Ba^{2+}$  ions. The selectivity behavior can be explained by the formation of a pseudo-cryptand structure pursuant to the overlapping of two CHQ groups. Hence, more stable  $K^+–2$  and  $Ba^{2+}–2$  in

comparison to complexes of **2** with the alkali and alkaline earth cations are facilitating the selective collection of those ions [101].

The SPE materials with specific recognition capability are attached with any of the following support options, e.g., silica gel, titania, zirconia or other polymers. Silica gel is used mostly among the support materials due to its high hydrophilic character, large number of binding sites and substantial inert nature. Other options are adopted only when the silica gel cannot be used as the support such as, when the pH of solution is above 10 or when extreme purification of water is required, etc. [105, 130]. The silica gel-bound macrocycles having different element-selective properties and behaviors can be prepared as shown in the Fig. 5 as described in detail by Bradshaw et al. [125]. Macrocycle containing SPE-materials possesses a greater concentration of active sites compared to the conventional element-separation option in solid-phase as attributable to the enmeshed small microporous particles into the microfibrinous matrix. The approach also eliminates the channeling effect that recurrently appeared with packed-bed SPE processes [105, 131].

## **5.0 Applications and Limitations of SPEs with molecular recognition plus macrocycles in element-separation**

### ***5.1 Applications***

#### ***5.1.1 Selective separation of toxic elements***

The macrocycle-immobilized SPEs are used for the separation of a single or a group of toxic elements from the solution matrix. Advanced application of such SPE systems for inorganic analysis of the harmful elements was discussed elsewhere [132], and, hence, the section highlights the other related instances of molecular recognition dependent SPE-application.

The selective separation of lead from a high matrix electroless waste solution was achieved with the macrocycle-immobilized SPEs, namely, AnaLig Pb-01 and Pb-02 [133]. The AnaLig Pb-02 has also been used for the measurement of precise lead isotope ratio and its application to geochemical reference samples [134], or in the scheme of spectrophotometric lead determination in solution using 4-(2-pyridylazo)-resorcinol [135]. Furthermore, the macrocycle-immobilized Pb-selective SPEs have been successfully applied for the separation/preconcentration of lead from biological and environmental samples [132, 134, 136-140].

A combination of SPEs containing immobilized macrocyclic material, namely AnaLig TE-01, AnaLig AN-01 Si and AnaLig As-01 PA, was used for selective separation of water-soluble arsenic species: arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid [141]. A simple flow-based method was also developed for the discerning separation of tri- and pentavalent arsenic species from aqueous matrix using another macrocycle-immobilized SPE, specifically AnaLig An-02 [142]. The selectivity characteristics of AnaLig TE-01 towards arsenic [141] and iron-species [143] were further employed to formulate an approach for the treatment of spent iron-oxide coated sand from filters used in arsenic removal [144].

The application of silica gel-bound macrocycle systems for the selective separation of cadmium [145] from the metal-affluent matrix, or hexavalent chromium from the wastewaters [146] and conversion coatings [147] has been reported.

Selective separation of the ecotoxic transition metal ions (e.g., Co, Ni, Cu, Zn, Cd) from aqueous solutions was achieved using immobilized macrocyclic material containing a solid phase extraction system, namely AnaLig TE-05 [148, 149]. The AnaLig TE-01 SPE system was used for the nondestructive recovery of multiple elements, such as, As(V), Cd(II), Cr(III), Pb(II) and Se(IV), from the effluent containing excess aminopolycarboxylate chelant in solution [150, 151].

### 5.1.2 *Selective separation of rare and precious metals*

There are some non-ferrous metals, which are termed as *rare metals* due to the economic or technological difficulty in acquiring those metals in abundance, that are highly essential in a wide range of manufacturing areas, including machineries and electronics production. The SPE-systems with molecular recognition capabilities have been used for the recovery of *rare-termed* metals (e.g., indium) from the end-of-life e-waste [152] or from the waste effluent from the production process [153]. The macrocycle-immobilized AnaLig PM-series SPE systems have been used for the selective recovery of the precious metals, such as, Pt, Au, Pd [154, 155].

### 5.1.3 *Selective separation of radioactive elements*

The application of macrocycle-containing SPE-systems has been used for the separation of uranium from nuclear power plant waste [156]. The use of various SPE-systems with the selectivity to various radioactive elements, such as, Sr, Tc, Cs and Ra has also been reported [157-164] and evaluated for large-scale applications [164-167].

## 5.2 *Limitations*

The macrocycle-immobilized SPEs with molecular recognition competence are available typically from the commercial sources in recent days. Although the mass production approach creates the prospect of cost-minimization in the process of research, the patent-obligation decreases the option for detail appraisal of the product and opportunity of suggesting any enhancement or further development. Therefore, a particular SPE-system can be evaluated for a certain separation application while the working mechanism remained unexplained creating the inadequacies of the use of SPEs with selective recognition property in element-separation.

Moreover, the detail potential of the commercial SPE-product that claimed to have recognition selectivity towards a single element or group of elements is sometimes either not

included in detail in the brochures or seldom verified from the researchers having no competing interest. For example, Hasegawa et al. [153] proposed the application of the macrocycle-immobilized AnaLig TE 02 SPE for the quantitative separation of the indium or tin from the etching waste solution of the flat-panel display fabrication process after a comparative evaluation with other similar SPE-types (AnaLig TE 03, AnaLig TE 07, AnaLig TE 13 and AnaLig PM 02). The likely application prospect of AnaLig TE 02 SPE does not include the possibility of such separation in the product brochure though.

## **6.0 Conclusion**

The industrial endeavors are ever-increasing and a simultaneous adoption of stringent regulation rules to restrict the likely environmental consequences from the process effluent or discards will, therefore, create a huge market-demand for the element-specific separation approaches. The SPEs with the advantage of molecular recognition can be better utilized for the selective separation of environmentally hazardous or economically viable elements from the waste resources. Furthermore, the SPE-technique has the benefit of easy-automation, and the process can be coupled with suitable systems to achieve the benefit of recovery and recycling. The trends towards the SPE-material development having enhanced selectivity features will thus be expected to be continued, and anticipated to be considered as an indispensable part of the traditional research and development section of the companies in the forthcoming eras. We expect the development of innovative waste-treatment methodologies in conjunction with such SPE systems in the future.

## **Acknowledgment**

This work was partially supported by the Grants-in-Aid for Scientific Research (24310056 and 24-02029) from the Japan Society for the Promotion of Science.

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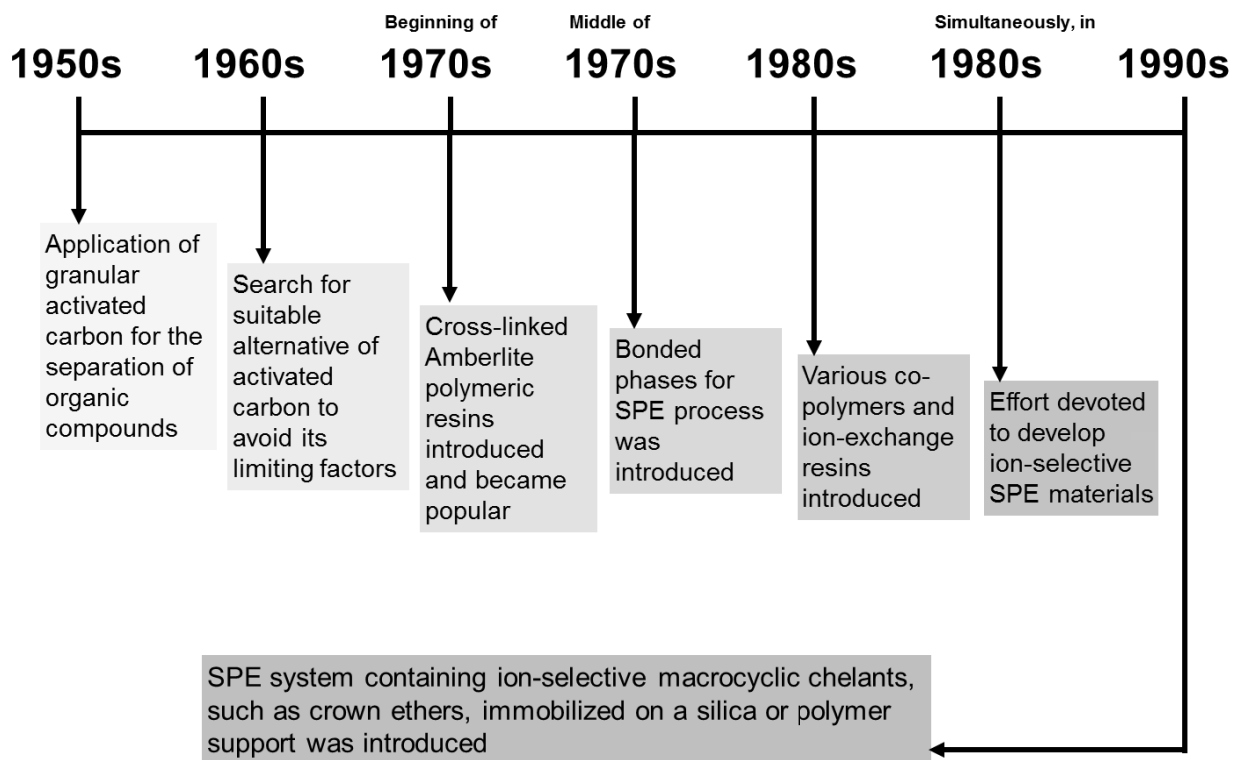
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**Table 1:** Comparative characteristics of the parent macrocycles

Macrocycle	Major guest	Structural diversity <sup>a</sup>	Guest selectivity <sup>a</sup>
Crown ether	Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> Ba <sup>2+</sup> , Ag <sup>+</sup> , Pb <sup>2+</sup> NH <sub>4</sub> <sup>+</sup> , RNH <sub>3</sub> <sup>+</sup>	A	A
Macrocyclic polyamine	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> polyanion	A	B
Macrocyclic polysulfide	Ag <sup>+</sup> , Pb <sup>2+</sup>	C	A
Cyclic peptide	Ca <sup>2+</sup> , Ba <sup>2+</sup> Cu <sup>2+</sup> , Zn <sup>2+</sup>	C	B
Calixarene	Na <sup>+</sup> , K <sup>+</sup> , Cs <sup>+</sup> Organic substrate	A	B
Cyclophane	Organic substrate	C	C
Cyclodextrin	Organic substrate	B	C

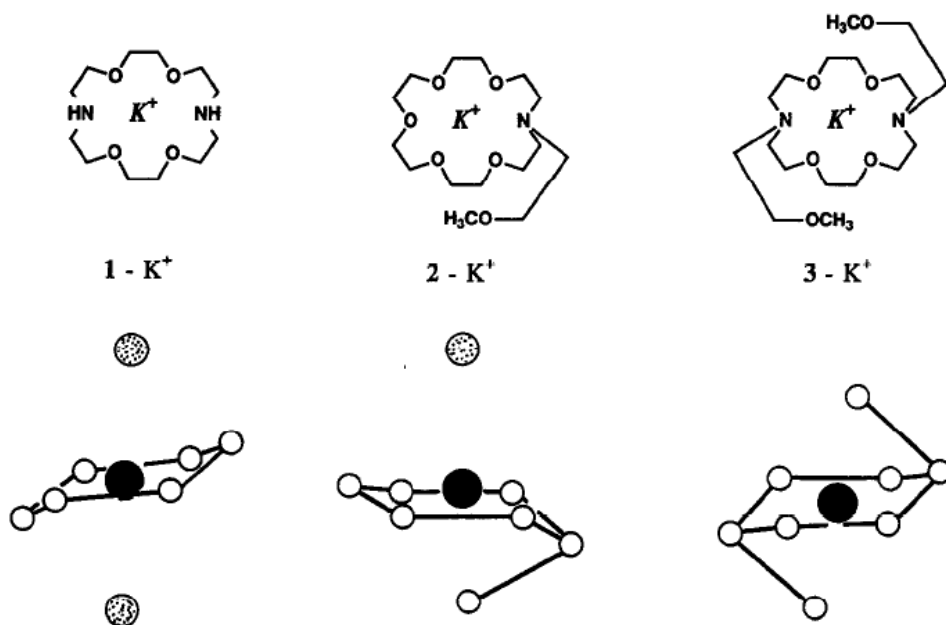
<sup>a</sup> *A: excellent, B: fair, C: not good.*

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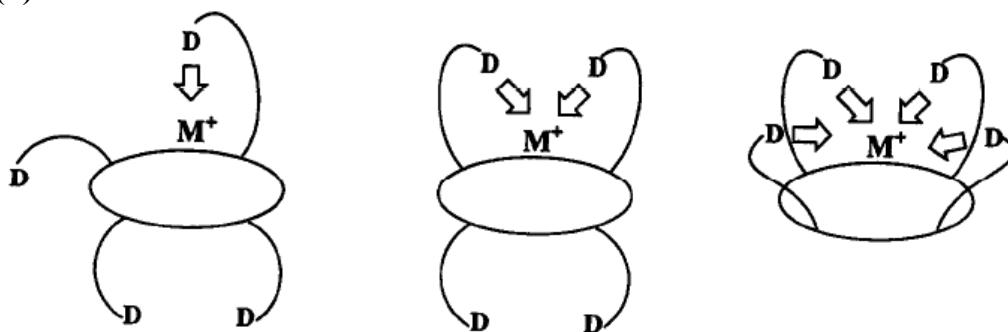


**Figure 1.** The development in SPEs until the introduction of macrocycle-containing SPEs: A timeline view.

(a)



(b)

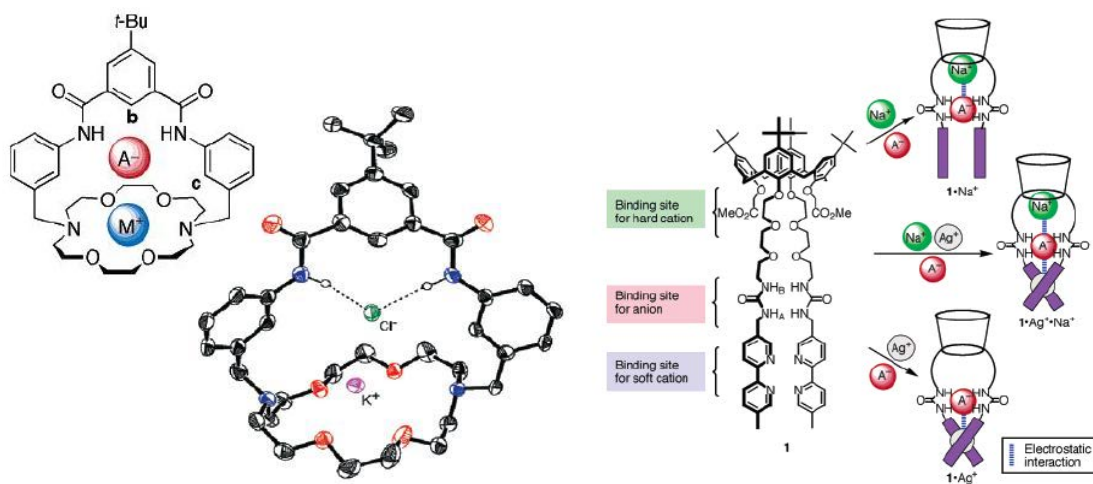


**Figure 2.** (a) Crystal structures of KI complexes with diaza-crown ether **1**, lariat ether **2**, and double armed crown ether **3**, (b) cation binding of armed macrocycles.

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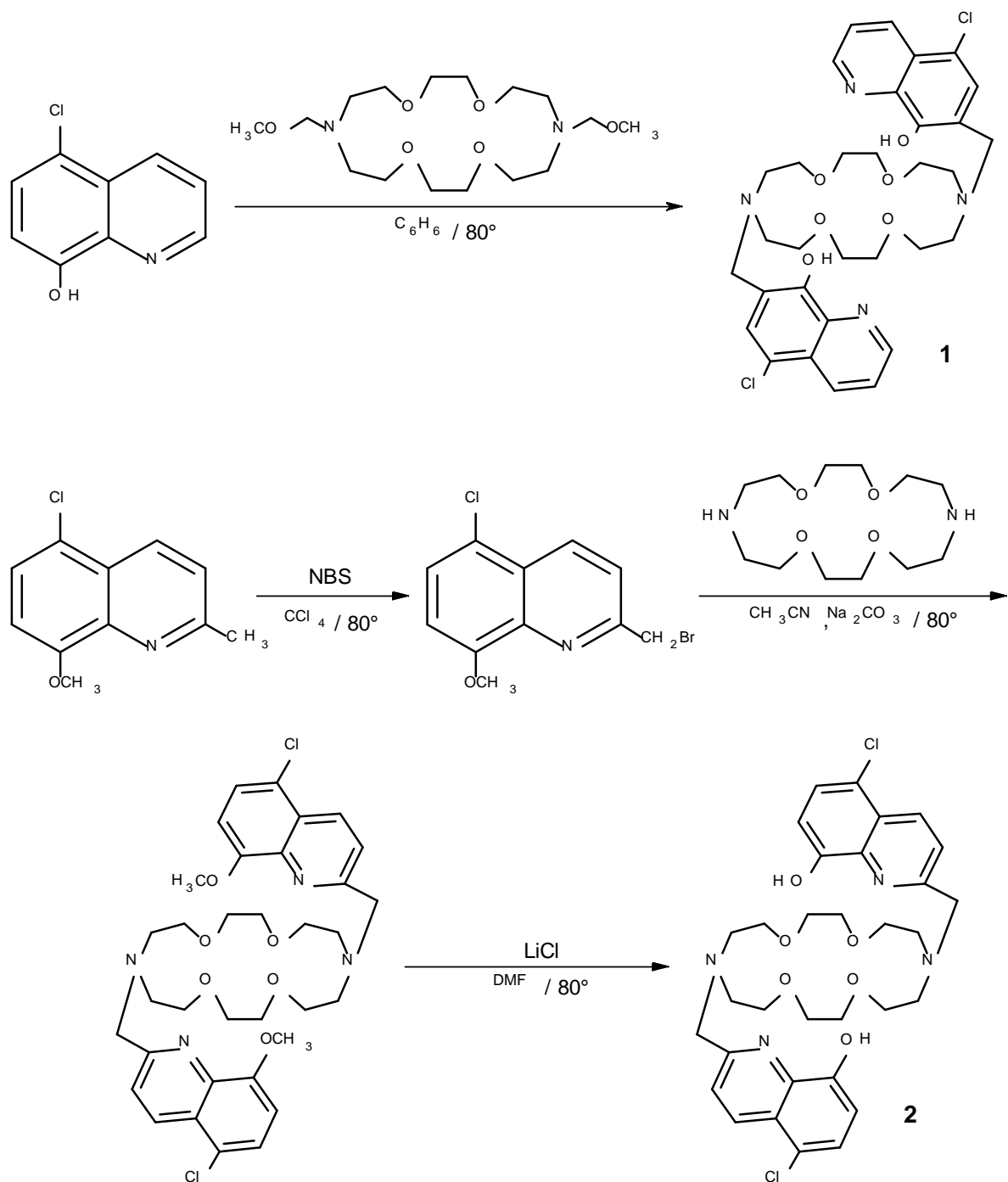
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**Figure 3.** Macrocyclic compounds with diverse selectivity options: (a) a macrobicyclic host structure that can accommodate both anion and cation species, (b) a multi-responsive host in which three different ion binding sites are arranged in a single structure.

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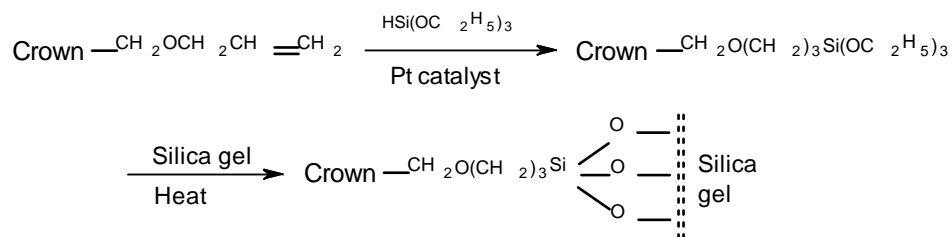


**Figure 4.** Scheme for the preparation of 5-chloro-8-hydroxyquinoline-substituted diaza-18-crown-6 macrocycles.

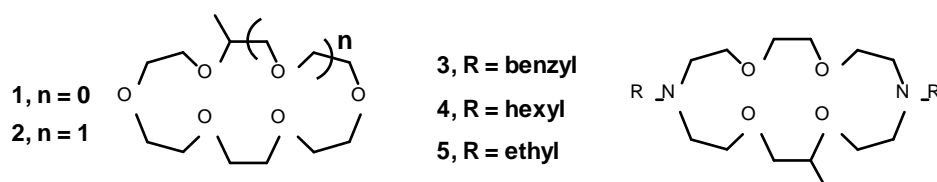
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**Crown Substituents**



**Figure 5.** Scheme for the preparation of silica gel-bound crown compounds

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