



Novel efficient functionalized tetrapyrazolic macrocycle for the selective extraction of lithium cations



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ABSTRACT

The synthesis of a new functionalized tetrapyrazolic macrocycle with two bidentate bipyrazolic subunits and a lipophilic moiety bearing a donor-group is described. The complexing properties of this macrocycle towards the alkali metal ions (Li^+ , Na^+ , K^+ , Cs^+) were studied by liquid–liquid extraction, and they showed a good extraction ability for Li^+ and Na^+ , and a remarkable selectivity for the lithium cation in competitive conditions.

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1. Introduction

Alkali metals extraction from aqueous and solid mediums is one of the most important industrial topics,¹ in particular, the selective extraction of the lithium salts, which presents high potential applications in different technologies and medicinal research.² In fact, lithium salts are among the most frequently used drugs for bipolar disorder patients.³ Recent studies suggest that lithium could also be used for the treatment of schizophrenia and Alzheimer's disease.⁴ The small lithium cations are strongly solvated in water, and their selective extraction from natural aqueous media such as seawater is difficult because of their coexistence with an excess of sodium cations, which present similar properties to the lithium cations, but are more weakly hydrated than Li^+ . In this regard, major efforts have been made to develop synthetic receptors allowing the selective extraction of lithium salts from an aqueous liquid phase into an organic liquid phase.⁵ The first synthesized Li^+ selective ionophores were the 14-crown-4 and 12-crown-4 derivatives.⁶ Most of them have been studied as Li^+ selective sensing electrodes.^{7–9} It was also reported that the association constants of spherand derivatives with lithium picrate in chloroform were several hundred-fold greater than those with sodium picrate in the same solvent.¹⁰

However, the spherands are not expected to present a good Li^+ selectivity in the solvent extraction system, due to the high Li^+ hydration in the aqueous phase compared to Na^+ . Another class of polydentate *sp*² hybridized nitrogen donor macrocycles based on polypyridine¹¹ and mixed pyridine-imine¹² ligands were developed and form highly stable complexes with lithium cations. Recently, we developed in our laboratory, different polypyrazolic macrocycles for the extraction, transport and release of lithium and alkali metal cations.^{13–16} These polypyrazolic macrocycles can also form stable complexes with transition metal cations such as Ru (II).^{17–22} The prepared macrocycles^{13–16} showed a pronounced selectivity to extract and transport the alkali metals (Li^+ , Na^+ and K^+), however, they present a limitation which consists in their migration from the organic phase to the aqueous solution during liquid–liquid extraction due to their dissolution in the aqueous phase. In order to overcome this inconvenient problem, we report the macrocycle **1** with a hydrophobic arm to prevent its dissolution in the aqueous phase during liquid–liquid extraction. In this paper, we describe the synthesis of a novel functionalized tetrapyrazolic macrocycle **1** (Fig. 1) with two bidentate bipyrazolic entities and its extraction properties towards alkali metal cations Li^+ , Na^+ , K^+ and Cs^+ . The presence of the *p*-phenylethyl hydroxy group on the side arm of macrocycle **1** gives a rigid structure to the macrocycle which allows a high selectivity among substrates with different sizes²³ and also overcome its migration limit as reported above.

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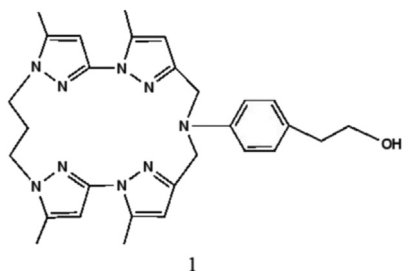


Fig. 1. Structure of macrocycle 1.

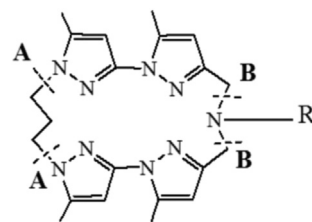


Fig. 2. Synthesis strategies of the macrocycle 1.

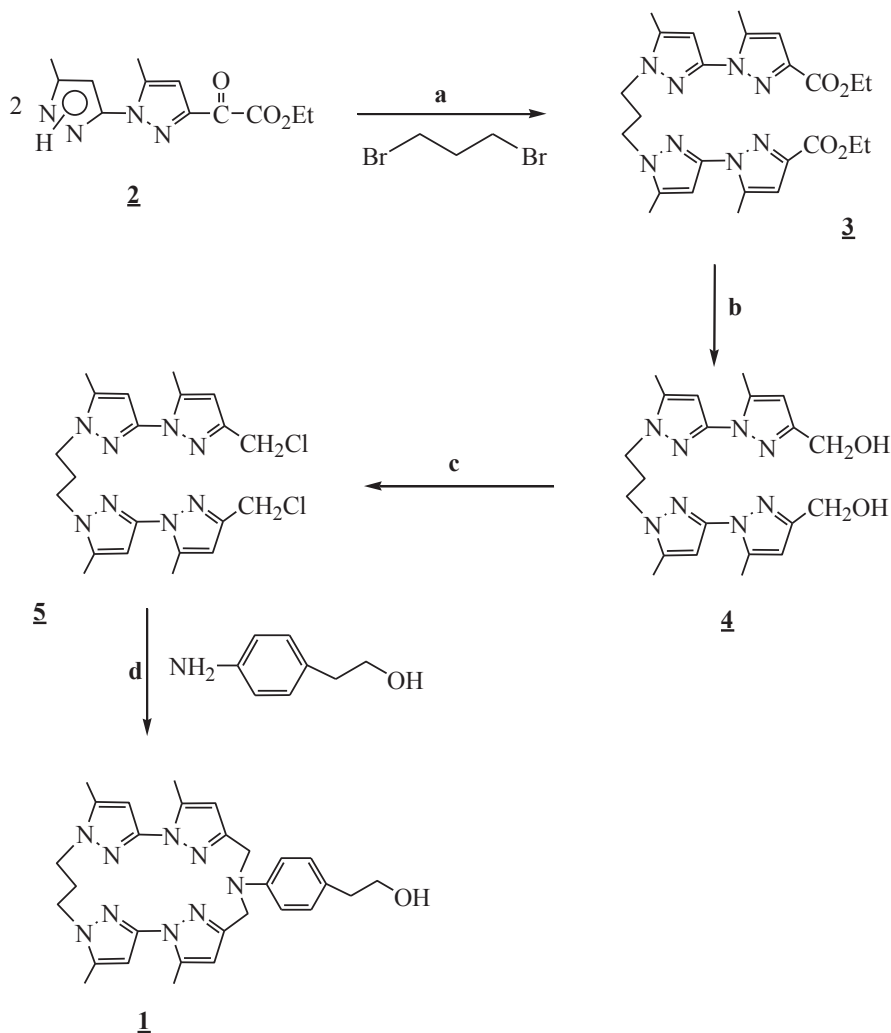
2. Results and discussion

2.1. Synthesis of the macrocycle 1

The synthesis of macrocycle **1** was performed by two different pathways as shown in Fig. 2. The pyrazolic macrocycle **1** can be obtained by the creation of two bonds [A] followed by two bonds [B] (route I) or conversely [B] followed by [A] (route II).

Our interest consists in determining of the most convenient and high yielding procedure, with the minimum the steps, to obtain the desired pyrazolic macrocycle **1**.

2.1.1. Route I. The synthesis of macrocycle **1** is shown in Scheme 1. The reaction of synthon **2**²⁴ with 1,3-dibromopropane was carried out in the presence of potassium *tert*-butoxide (*t*BuOK) as a strong base, to afford product **3** resulting from the α - α attack, as the major isomer according to the method generally used to differentiate the obtained isomers.²⁵ Then, compound **3** was reduced in the presence of lithium aluminum hydride to give dihydroxyl product **4** in 75% as yield. The action of thionyl chloride on compound **4** give chlorinated derivative **5** in 80% as yield and the final step was the creation of two bonds 'B' (Fig. 2) by condensation of the compound **4** with 2-(4-aminophenyl) ethanol in acetonitrile and under high



Scheme 1. Synthesis of the macrocycle **1** following the route I. Reagent and conditions (a) *t*BuOK, THF, Reflux, 15 h, 65% (b) LiAlH₄, THF, Reflux, 6 h, 75% (c) SOCl₂, CH₂Cl₂, RT, 12 h, 80% (d) Na₂CO₃; CH₃CN, Reflux, 24 h, 54%.

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