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Improvement of the extraction ability of bis(2-propyloxy)calix[4]arene-crown-6 toward cesium cation by introducing an intramolecular triple cooperative effect

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ABSTRACT

Bis(2-propyloxy)calix[4]arene-crown-6 (**L1**) is a ligand with high affinity in the extraction of Cs(I). In this work, acrylamido and propionamido groups are decorated at the opposite site of 2-propyloxy on the phenyl ring of **L1**, giving rise to the derivatives **L2** and **L3**, respectively. Complexation of all the three ligands with Cs(I) is characterized by NMR, spectrophotometric titration, crystal structure and DFT calculation. Both the NMR and spectrophotometric analysis suggest more significant variation of electron density on the phenyl rings in **L2** and **L3** than that in **L1** in complexation with Cs(I). The stability constants (logβ) of the complexes are calculated to be 6.0 ± 0.1, 6.2 ± 0.1 and 6.3 ± 0.1 for Cs-**L1**, Cs-**L2** and Cs-**L3**, respectively, by fitting of the absorption spectra. As reflected by the crystal structures and DFT calculations, the complexed cesium cation interacts with the crown ether moiety, the two rotated phenyl rings and the acrylamido/propionamido groups in **L2**/**L3**, which can be regarded as an intramolecular triple cooperative effect. Extraction of Cs(I) from aqueous solution is performed, and the distribution ratio is in line with the findings in stability constant and interaction energy. This work contributes to further improvement of the extraction of cesium cation by 1,3-alternate calix[4]arene-crown-6.

1. Introduction

The reprocessing and safe management of spent nuclear fuel is of great importance and also a challenge work all over the world. Cs-137 is radioactive and heat-emitting, which is a troublesome isotope in HLLW. Removal of Cs-137 prior to waste vitrification can reduce the waste volume and minimize the long-term hazards [1]. Liquid-liquid extraction is an efficient method to separate Cs-137 from HLLW, in which use of an appropriate extractant is very crucial. The class of 1,3-alternate calix[4]arene-crown-6 has been demonstrated to be promising, among which bis(2-propyloxy)calix[4]arene-crown-6 (**L1**, the structure is shown in Fig. 1) has been successfully applied in processing of real HLLW at institute of nuclear and new energy technology (INET) in Tsinghua University [2,3]. Besides, 1,3-alternate calix[4]arene containing two crown ether bridges, i.e., calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (BOBCalixC6) is the extractant for the well-known CSSX (caustic-side solvent extraction) process for extraction and separation of cesium cation from alkaline HLLW. Bruce A. Moyer and coworkers have done an excellent work in pioneering and developing the CSSX process [4,5]. Besides liquid-liquid extraction, other techniques such as extraction chromatographic technique based on ion exchanges and adsorbents using calix[4]arene-crown-6 as ligands were also developed for removal of radioactive cesium cation [6–8].

The reason why calix[4]arene-crown-6 have such an extraordinary extraction ability to cesium cation can be explained by an intramolecular cooperative effect in its coordination behavior with cesium cation, that is, a combination of metal-oxygen and cation-π interactions [9]. Cesium cation interacts not only with the crown ether moiety (metal-oxygen interaction) but also with the two rotated phenyl rings (cation-π interaction). Moreover, it has been confirmed that the binding efficiency of calix[4]arene-crown-6 derivatives with cesium cation is substantially affected by the nature of substituent groups. Appropriate derivatization of calix[4]arene-crown-6 for enhancing the affinity as well as the applicability of recognition of cesium cation is still a topic of current interest. Up to now, there have been a large number of reports on the effort mainly devoted to changing substituent group on the phenyl ring, decorating the ether chain, and changing the donor atoms to modify the affinities of calix[4]arene-crown-6 [10–14].

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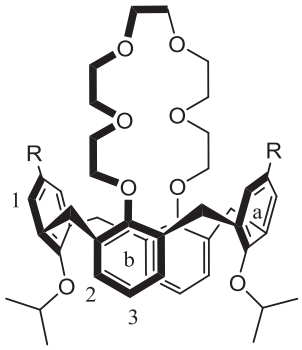

L1 R = H
L2 R = NHC(O)CHCH$_2$
L3 R = NHC(O)CH$_2$CH$_3$

Fig. 1. Structure of bis(2-propyloxy)calix-crown-6 (**L1**) and its derivatives.

For example, Sachleben and coworkers compared the distribution ratios and selectivities of didehydroxylatedcalix[4]arene-crown-6 and 1,3-dialkoxycalix[4]arene-crown-6 in liquid-liquid extraction of cesium [10]. The later one exhibits higher distribution ratio of Cs(I), indicating the substituent group on the phenyl ring can influence the extraction performance. Conformational and electronic factors are considered to be responsible for the different ionophoric properties of calix[4]arene-crown-6.

It must be mentioned that, in the modification of substituent group on the phenyl ring, previous reports were mainly focused on the effect of substituent group at the lower site on the two rotated phenyl ring (for example changing the 2-propyloxy group to other groups in **L1**, as shown in Fig. 1), whilst rare work were reported on decoration at its opposite site (the R group in Fig. 1). It is speculated that substituent group at site R can introduce two effects on complexation of calix[4]arene-crown-6 with cesium cation. One is the electronic effect on the cation-π interactions as mentioned above, and the other is considered as following. In the crystal structure of **LI** with cesium according to the literature [15,16], cesium locates in the cavity interacting with six oxygen atoms and the two rotated phenyl rings. The coordination of cesium is actually unsaturated, providing the opportunity for anions, including picrate (Pic^-) and bis(trifluoromethylsulfonyl)imide (NTf_2^-), to coordinate with cesium. Therefore, it is speculated that decoration of functionalized substituent group with appropriate donor atom at site R can further enhance the affinity of **L1** for cesium cation. As the complexation of cesium with **L1** is already an intramolecular cooperation, introducing another coordinating group can be regarded as an intramolecular triple cooperative effect. To the best of our knowledge, the report on decorating the site R in calix[4]arene-crown-6 is very rare. Korovitch et al. reported that presence of sulfonates at site R increased the affinity constants in the complexation of calix[4]arene-bis(crown-6-ether) with cesium due to the involvement of the sulfonate in complexation, which was analyzed by quantum chemical calculations [11]. Unfavorable to solvent extraction, however, presence of sulfonate group greatly enhanced the hydrophilicity of the ionophore [11,17].

In this work, we intend to investigate the effect of substituent group at site R of **L1** on the complexation and extraction of cesium cation. In one of our previous studies, we have synthesized 11,23-diacrylamido-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (**L2**) with the purpose to graft the ligand **L1** on microspheres to absorb Cs(I) from aqueous solutions [6]. The absorption is efficient, but the complexation behavior of **L2** with Cs(I) is still remained to be discovered. Furthermore, we herein synthesized a new calix[4]arene-crown-6 derivatives, i.e., 11,23-dipropionamido-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (**L3**). The complexation behavior of these two ligands as well as **L1** with cesium cation are exploited in this work by use of NMR, spectrophotometric titration, single crystal structures, DFT calculations, and liquid-liquid extraction study. We speculated that appropriate modification of the substituent group at site R of **L1** would further enhance its affinity in the complexation and extraction of cesium cation. And we also hope that this work would contribute to further understanding of the complexation of 1,3-alternate calix[4]arene-crown-6 with cesium cation.

2. Experimental section

2.1. Materials

The calix[4]arene crown ether **L1** was produced at INET, Tsinghua University, China, at a purity of more than 99.5%. Cesium salts and $HNTf_2$ were purchased from Sigma-Aldrich. $C_2mimNTf_2$ was purchased from J&K Scientific Ltd., China. $CsNTf_2$ was synthesized via a neutralization reaction with equal mole of CsOH and $HNTf_2$ in water. All the chemicals used in this work were of analytical grade and used without further purification.

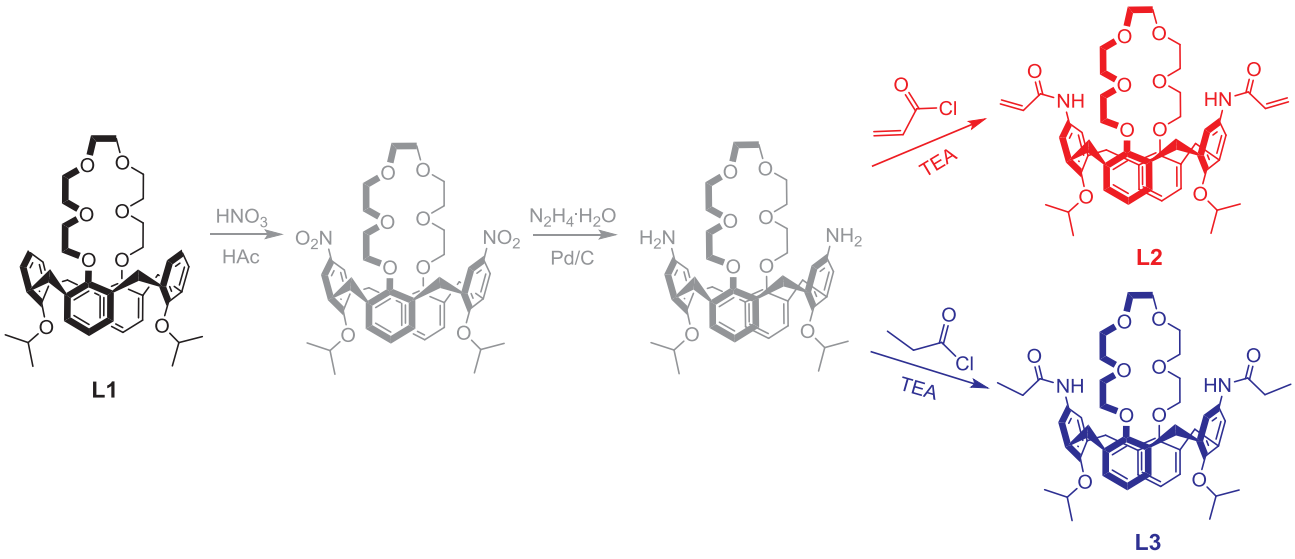

Fig. 2. Synthetic route for the calix[4]arene crown derivatives.