

## Voltammetric Behavior of Nano-basket Complexes

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Eight nano-baskets of cone calix[4]arene-crown-3, -crown-4, -crown-5, -crown-6 were synthesized and their binding abilities towards alkali and alkaline earth metals as well as some lanthanides were studied using differential pulse voltammetry. The novelty of this study was investigation of those nano-basket complexes by voltammetric behaviors of two acidic moieties in each scaffold during complexation of crown ether ring. Their voltammetric behaviors were closely related to the complex formation by entrapment of cation into crown ether cavity and ion-dipole interaction between cation and acidic moieties in nano-baskets. The results revealed the selective changes in voltammetric behavior of synthesized scaffolds toward the cations. By increasing the binding ability of macrocycle and cation, the anodic oxidation peak of carboxylic acids was decreased. It was shown that the voltammetric traces of low energy complexes did not affected by encapsulated cations in the coordination space of crown ether and they showed no voltammetric behavior.

**Keywords:** Nano-baskets, Differential Pulse Voltammetry, Calixcrown, Upper Rim.

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### 1. INTRODUCTION

Nano-baskets of calixarenes and calixcrowns are a versatile class of macrocycles, which have been subject to extensive research in development of many extractants [1-5]. Functionalization of calix[4]arenes at both the upper rim and the lower rim has been extensively studied. Attaching donor atoms to the lower rim of a calix[4]arene can improve the binding strength of the parent calixarene dramatically. The two main groups of lower rim functionalized calix[4]arenes are calix[4]arene podands and calixarene-crown ethers [6,7]. Distal hydroxyl groups can be connected to give 1,3-bridged calix[4]crowns, while connection between proximal hydroxyl groups leads to 1,2-bridged calix[4]crowns.

It is found that the 1,3-bridged calix[4]crowns exhibit high binding affinity and selectivity toward alkali and alkaline earth metal cations [8], while the researches on 1,2-bridged calix[4]crowns lag far behind. Combining crown ethers with calix[4]arenes increases the cation binding ability of the parent calixarenes, and control of the selectivity is obtained through modulation of the crown ether size. Attachment of proton-ionizable groups to calixcrowns can further improve their extraction properties because the ionized group not only participates in metal ion coordination, but also eliminates the need to transfer aqueous phase anions into the organic phase. Ungaro et al. [9] reported the first di-proton-ionizable calix[4]crown-5 in 1984 and it showed quite high efficiency in extraction of divalent cations from water into dichloromethane. Combining crown ethers with calix[4]arenes increases the cation binding ability of the parent calixarenes [10-12]. In this work, eight diacid proton-ionizable calixcrowns were

synthesized including cone *p-tert*-butyl-25,26-di(carboxymethoxy) calix[4]arene1,2-crown-3 (10), cone *p-tert*-butyl-25,26-di(carboxymethoxy) calix[4]arene1,2-crown-4 (11), cone *p-tert*-butyl-25,26-di(carboxymethoxy) calix[4]arene1,2-crown-5 (12), cone *p-tert*-butyl-25,26-di(carboxymethoxy) calix[4]arene1,2-crown-6 (13), cone 25,26-di(carboxymethoxy) calix[4]arene1,2-crown-3 (23), cone 25,26-di(carboxymethoxy) calix[4]arene1,2-crown-4 (24), cone 25,26-di(carboxymethoxy) calix[4]arene1,2-crown-5 (25), and cone 25,26-di(carboxymethoxy) calix[4]arene1,2-crown-6 (26). The voltammetric behavior of the synthesized scaffolds was determined using some alkali, alkaline earth, transition metals and lanthanides. Fig. 1 depicted the structure of eight calixcrown scaffolds as extractant agents.

### 2. EXPERIMENTAL

Voltammetric measurements were utilized by a Model 660 electrochemical workstation (CH Instruments, Austin, TX, USA) with a three-electrode cell including a Pt wire counter electrode, a glassy carbon working electrode and an Ag/Ag<sup>+</sup>(0.1 M) reference electrode, separated from the solution by a plug. The surface of the glassy carbon electrode was polished using 0.3 μm alumina (Buehler, Lake Bluff, MN) and residual alumina particles were thoroughly removed by placing the working electrode in an ultrasonic cleaner for 20 min and was dried and washed with pure acetonitrile. 0.1 mM calixcrowns and stock solution of metal perchlorate salts with various concentrations were prepared using acetonitrile. 0.1 M tetra-n-butylammonium hexa-fluorophosphate (TBAPF<sub>6</sub>) was used as supporting electrolyte.

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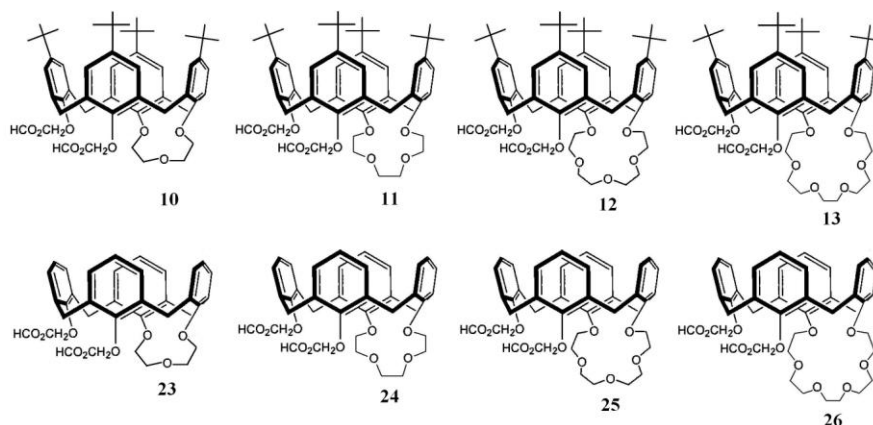


Fig. 1 – The chemical structure of eight calixcrown scaffolds were synthesized and studied

### 3. RESULTS AND DISCUSSION

The complexation of 0.1 mM compounds 10 – 13 and 23 – 26 towards various cations (including alkali, alkaline earth, transition metals and lanthanides) were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at glassy carbon electrode in 0.1 M TBAPF<sub>6</sub>/acetonitrile solution. According to Fig. 2, CVs of host macrocycles show almost same voltammetric behavior which is no reduction peak and two anodic peaks at 0.8 and 1.4 V in scaffolds 23 – 26, and 0.9 and 1.3 V in scaffold 10 – 13, respectively.

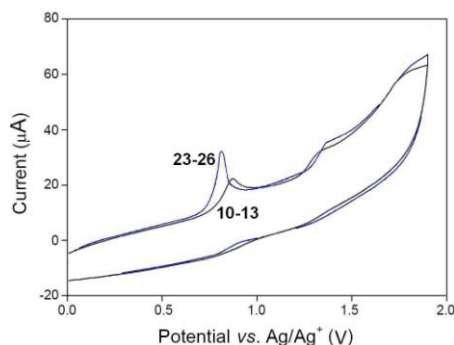


Fig. 2 – Cyclic voltammograms of 0.1 mM 10 – 13 and 23 – 26 at glassy carbon working electrode.

This phenomenon is related to the redox behavior of carboxylic acids and intramolecular H-bonding (between two of carboxylic acid groups) in 10 – 13 and 23 – 26. Although the oxidation of carboxylic acid exhibits one oxidation peak with two electron and proton transfer in organic solution, the formation of intramolecular H-bonding between two carboxylic acids in 10 – 13 and 23 – 26 causes one proton transfer easier and the other more difficult, leading to oxidation peaks at a more positive potential and a less positive potential, respectively. Oxidation behavior of two carboxylic acid groups in 10 – 13 and 23 – 26 implies that H-bonding to carboxylic acid moiety is influenced by binding to cations because the carboxylic acids are located around the crown ether moiety.

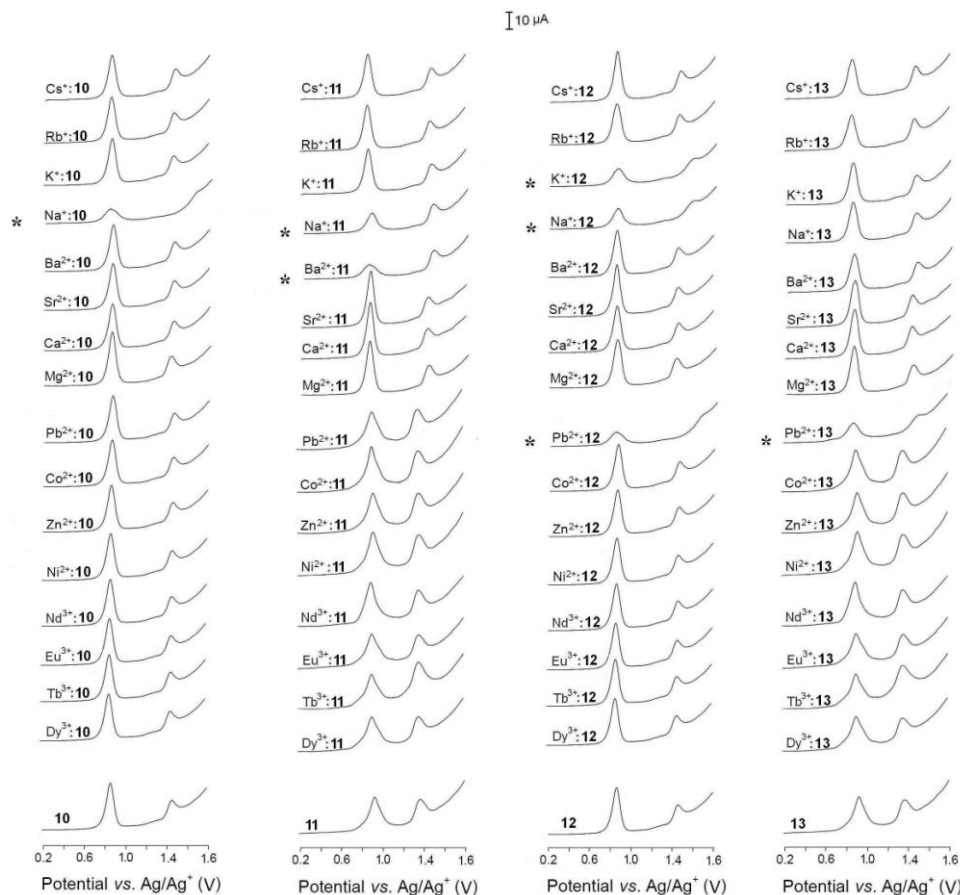
In the rest of the experiments, DPV was used instead of CV to get a better resolution of waves in the same condition. The voltammetric behaviors of carboxylic acids in each host scaffolds were compared with

different cations in DPV to investigate the binding properties of 10 – 13 and 23 – 26.

A constant volume of 10 µL per injection of the cation in 0.1 M TBAPF<sub>6</sub> was added into the cell to make 0.1 – 3.0 equivalent of cation in the solution. DPVs were recorded after adding stoichiometric equivalent of cations successively to the respective electrochemical solution. DPVs of 10 – 13 and 23 – 26 depict almost same voltammetric behaviors with two anodic peaks, as indicated in CV. Fig. 3 presented the differential pulse voltammograms of 0.1 mM 10 – 13 in the presence of 0.1 mM alkali, alkaline earth, transition metals and lanthanides in CH<sub>3</sub>CN.

As depicted in the first column of Fig. 3, the macrocycle 10 in the presence of Na<sup>+</sup> shows significant voltammetric changes of DPV in both the peak current and the potential. This is due to the electrostatic interaction between 10 and the cations, leading to electrostatic perturbation of intramolecular H-bonding by encapsulation of Na<sup>+</sup> into crown ether and two carboxylic acid groups. According to the second column of Fig. 3, by addition of one equivalent of alkali, alkaline earth, transition metals and lanthanides to a solution containing macrocycle 11, no changes were observed in the peak current or potentials except for Na<sup>+</sup> and Ba<sup>2+</sup>. Based upon the third column of Fig. 3, addition of one equivalent of K<sup>+</sup>, Na<sup>+</sup>, Pb<sup>2+</sup> to 12 caused large decrease in anodic peak currents or even disappearance of the original second anodic peak. This behavior is related to the electrostatic perturbation of intramolecular H-bonding by binding of cations into crown ether and two carboxylic acid groups. As presented in the fourth column of Fig. 3, by addition of one equivalent of selected cations to macrocycle 13, no changes were observed in both the peak current and the peak potentials except for Pb<sup>2+</sup>.

Regarding to the role of binding site in the complex, the crown ether groups of 10 – 13 (and 23 – 26) act mainly as landing sites for cations, while the carboxylic acid groups constitute the redox active centers as well as the supporting landing sites for binding. The inclusion of divalent metal ions by the crown loop (and hydroxyl groups of carboxylic acids) may cause deprotonation of carboxylic acids, which makes it difficult to oxidize carboxylic ion to carboxy radical in the oxidation process.



**Fig. 3** – Differential pulse voltammograms of 0.1 mM 10 – 13 in the presence of 0.1 mM alkali, alkaline earth, transition metals and lanthanides in CH<sub>3</sub>CN.

The reason is contributed to the repulsion between the carboxy radical and the positive cations in scaffolds 10-13 and 23-26. The peak height changes of the first oxidation potential of one equivalent of 10-13 and 23-26 in the presence of one equivalent of different cations are tabulated in Table 1. The current decreasing orders of 10 – 13 and 23 – 26 of the first peak are Na<sup>+</sup> for scaffold 10, Na<sup>+</sup> < Ba<sup>2+</sup> for

scaffold 11, Na<sup>+</sup> < K<sup>+</sup> < Pb<sup>2+</sup> for scaffold 12, Pb<sup>2+</sup> for scaffold 13, Na<sup>+</sup> for scaffold 23, Ba<sup>2+</sup> for scaffold 24, K<sup>+</sup> < Ba<sup>2+</sup> for scaffold 25, and Ca<sup>2+</sup> < Pb<sup>2+</sup> for scaffold 26 that are in accordance with the order of potential shifts ( $\Delta Ep_2 = Ep_2^* - Ep_2$ ), which are tabulated in Table 2.

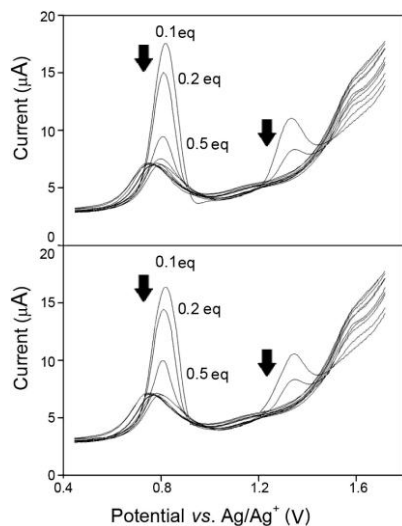
**Table 1** – The changes of current ratio in the first anodic peak for complexation of 0.1 mM scaffolds 10 – 13 and 23 – 26 with the 0.1 mM solutions of different metal perchlorate salts in CH<sub>3</sub>CN

macrocycle	Cs <sup>+</sup>	Rb <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ba <sup>2+</sup>	Sr <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Pb <sup>2+</sup>	Co <sup>2+</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>	Nd <sup>3+</sup>	Eu <sup>3+</sup>	Tb <sup>3+</sup>	Dy <sup>3+</sup>
<b>10</b>	0.89	0.92	0.94	<b>0.43</b>	0.88	0.96	0.95	0.99	0.90	0.96	0.99	0.94	0.98	0.98	0.99	0.99
<b>11</b>	0.88	0.90	0.88	<b>0.56</b>	<b>0.47</b>	0.94	0.96	0.99	0.96	0.98	0.99	0.98	0.99	0.98	0.99	0.99
<b>12</b>	0.92	0.92	<b>0.41</b>	<b>0.48</b>	0.92	0.89	0.90	0.96	<b>0.37</b>	0.88	0.86	0.92	0.94	0.95	0.98	0.98
<b>13</b>	0.92	0.92	0.89	0.96	0.95	0.89	0.90	0.96	<b>0.44</b>	0.88	0.86	0.92	0.94	0.95	0.98	0.98
<b>23</b>	0.90	0.91	0.95	<b>0.51</b>	0.91	0.94	0.96	0.97	0.97	0.98	0.98	0.97	0.96	0.99	0.99	0.98
<b>24</b>	0.90	0.94	0.91	0.89	<b>0.44</b>	0.92	0.93	0.97	0.94	0.98	0.97	0.99	0.98	0.98	0.98	0.99
<b>25</b>	0.89	0.93	<b>0.42</b>	0.91	<b>0.39</b>	0.88	0.89	0.98	0.88	0.89	0.94	0.96	0.97	0.99	0.99	0.98
<b>26</b>	0.89	0.88	0.93	0.89	0.91	0.90	<b>0.58</b>	0.97	<b>0.49</b>	0.89	0.95	0.95	0.96	0.99	0.98	0.99

**Table 2** – Differences of peak potentials (mV) between free and complexed macrocycles 10-13 and 23-26 by DPV

macrocycle	Cs <sup>+</sup>	Rb <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ba <sup>2+</sup>	Sr <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Pb <sup>2+</sup>	Co <sup>2+</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>	Nd <sup>3+</sup>	Eu <sup>3+</sup>	Tb <sup>3+</sup>	Dy <sup>3+</sup>
<b>10</b>	15	13	10	<b>201</b>	11	6	8	2	12	5	1	11	2	5	3	2
<b>11</b>	12	16	7	<b>188</b>	<b>204</b>	5	12	2	16	6	3	4	0	3	2	2
<b>12</b>	5	9	<b>191</b>	<b>165</b>	7	18	12	6	<b>234</b>	14	15	9	3	1	0	4
<b>13</b>	5	9	3	9	6	18	12	6	<b>179</b>	14	15	9	3	1	0	4
<b>23</b>	13	8	6	<b>158</b>	11	7	6	4	5	6	2	9	6	4	4	3
<b>24</b>	14	12	7	6	<b>188</b>	7	10	0	9	7	4	3	1	2	3	2
<b>25</b>	11	5	<b>198</b>	6	<b>222</b>	14	10	8	12	8	10	10	4	2	2	3
<b>26</b>	14	12	6	3	12	6	<b>161</b>	0	<b>178</b>	5	11	8	5	4	2	2

Complexion behavior of 10–13 and 23–26 scaffolds with increasing amounts of corresponded cations was continued. Figure 4 depicted the effect of concentration of corresponded cations to scaffolds 10 and 23. With increasing the amounts of cations, the anodic peaks at 0.8 V and 1.4 V decreased. The peak current at 0.8 V decreased quantitatively by increasing the concentration of  $\text{Na}^+$ , and gradually reached to the minimum value at around one equivalent.



**Fig. 4** – Differential pulse voltammograms of 0.1 mM 10 (up) and 23 (down) with  $\text{Na}^+$  in  $\text{CH}_3\text{CN}$

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## 4. CONCLUSIONS

The voltammetric behavior of calix[4]crowns 10–13 and 23-26 and their binding abilities toward alkali, alkaline earth, transition metals and lanthanides were examined by differential pulse voltammetry. Compounds 12 and 25 showed their voltammetric behavior toward  $\text{K}^+$ , 10-12 and 23 towards  $\text{Na}^+$ , 11, 24 and 25 towards  $\text{Ba}^+$ , 26 towards  $\text{Ca}^{2+}$ , and 12, 13 and 26 towards  $\text{Pb}^{2+}$  in  $\text{CH}_3\text{CN}$ . This was mainly related to the presence of crown ether group between two proximal carboxylic acid moieties in the complex frameworks. Comparing of scaffolds 10–13 (tert-butyl as upper rim) with 23–26 (without upper rim) revealed that such complexes are formed in the lower rim, and the upper rim moieties have no remarkable effect on the lower rim complexation with cations.

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