The study of spectrographic properties and molecular recognition of calix[$n$]arenes

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Abstract

The absorption spectrum and fluorescence spectrum of calix[$n$]arenes are studied systematically. The self-association of calix[$n$]arenes is proposed and the self-association constant is also obtained. The recognition properties of calix[$n$]arenes are studied and the inclusion constant is calculated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The calix[$n$]arenes are macrocyclic compounds which are usually obtained by base-catalyzed condensation of $p$-alkylphenols and formaldehyde and are of interest as potential ligands and molecular hosts. To get good recognition properties, many derivatives of calix[$n$]arenes have been obtained [1–5], which can recognize metal ions and neutral organic molecules with good selectivity. With the development of the calixarene chemistry, calix[$n$]arenes have been applied in many areas such as catalysis, separation and determination [6–10]. Although scientists pay much attention to the calix[$n$]arenes derivatives and their recognition properties, the systematic study of the spectral properties of the mother molecules has not been reported.

In this paper, we describe the UV absorption spectrum and fluorescence spectrum of $p$-tert-buyl calix[$n$]arenes, de-butyl calix[4]arene and de-butyl calix[6]arene. From the spectrum, the association of molecules is proposed and the association constant is obtained. At the same time, the recognition properties of calix[$n$]arenes are also studied.

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2. Experimental

2.1. Apparatus

All fluorescence measurements were made with a Hitachi 850 spectrofluorometer. All absorption spectrums were recorded with an UV-240 spectrophotometer (Shimadzu).

2.2. Reagents and Materials

\( p\text{-}\text{tert}-\text{butyl} \) Calix[4]arene, de-butyl calix[4]arene and \( p\text{-}\text{tetra-butoxy} \) calix [4]arene are prepared from phenol according to literatures [11–13] and identified by IR and NMR. The debutyl calix[6] arene is kindly offered by Ms Quanli Ma, a doctoral student of Chinese Academy of Science (CAS). All the other reagents are of analytical-reagent grade.

2.3. Procedure

2.3.1. Study of the spectrum

The calix[\( n \)]arenes are solved into \( \text{NN-dimethylformamide} \) (DMF) and CHCl\(_3\) and then the UV absorption spectrum and fluorescence spectrum are determined.

2.3.2. Study of the recognition

Naphthoyl chloride is solved into DMF and then NaH is added into the solution. After removing the reductant NaH by filtration, the fluorescence is determined. Then, calix[\( n \)]arenes are added into the treated naphthoyl chloride-DMF and the fluorescence is determined. As a comparison, the naphthoyl chloride that is not treated with NaH is also studied.

3. Results and discussion

3.1. UV absorption spectrum of calix[\( n \)]arenes

The UV absorption spectrum of de-butyl calix[6]arene in DMF is shown in Fig. 1. From Fig. 1, it can be seen that the absorption spectrum has three absorption peaks, which lie in 261, 288 and 318 nm, respectively. The three peaks owe to 1B, 1La and 1Lb absorption band of benzene ring, respectively. The absorption in 288 nm is so strong that it almost covers up the third peak. It can also be seen that there is not evident change when the concentration of de-butyl calix[6]arene increases. The UV absorption spectrums of \( p\text{-}\text{tert}-\text{butyl} \) calix[4]arene, \( p\text{-}\text{tert}-\text{butyl} \) tetra-butoxy calix[4]arene and de-butyl calix[4]arene are similar with that of de-butyl calix[6]arene. The absorption peaks of calix[\( n \)]arenes are list in Table 1.

3.2. Fluorescence spectrum of calix[\( n \)]arenes

The fluorescence spectra of de-butyl calix[6]arene in DMF and CHCl\(_3\) are shown in Figs. 2 and 3, respectively. From Fig. 2, it can be seen that the maximum excitation wavelength lies in \(~\text{310 nm}\). With the increasing of the concentration, there is a bathochromic shift in the excitation wavelength. It can also be seen that the

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emission spectrum has two peaks in low concentration, but only one peak in high concentration. With the increasing of the concentration of de-butyl calix[6]arene, the two peaks increase at first, when the concentration is higher than $1.0 \times 10^{-4}$ mol/l, the second peak decreases and will disappear at last. The first peak also decreases when the concentration is higher than $5.0 \times 10^{-4}$ mol/l. From Fig. 3, it can be seen that the fluorescence spectrum of de-butyl calix[6]arene in CHCl₃ has only one emission peak. This indicates that there is an intermolecular interaction between de-butyl calix[6]arene and DMF. The fluorescence spectrum of the other calix[n]arenes are similar with that of the de-butyl calix[6]arene.

3.3. Self-association of the calix[n]arenes

Since de-butyl calix[6]arene has two emission peaks in DMF, which lie in 360 and 420 nm respectively, but has only one emission peak in CHCl₃, the wavelength of which (365 nm) is similar with the first emission peak in DMF, it can be supposed that the first peak owes to de-butyl calix[6]arene, but the second peak owes to the complex of de-butyl calix[6]arene and DMF. Additionally, when the concentration of de-butyl calix[6]arene is quite high, the fluorescence is quenched. It can be thought that there is a self-association between the calix[6]arene molecules.

Another evidence also supports the self-association supposition. According to Hosoya’s report [14], the $A \sim \log[c]$ curve will be an S-shaped curve when the aromatic compounds self associate and the association constant can be obtained from the $A \sim \log[c]$ curve. From Fig. 4, the $A \sim \log[c]$ curve of de-butyl calix[6]arene is an S shaped curve, which also indicates that there is a self-association in high concentration of calix[6]arene. From Fig. 4, the association constant of debutyl calix[6]arene can be obtained, which is $K_a = 7.9 \times 10^3$. The $A \sim \log[c]$ curves of other calixarenes are similar with that of de-butyl calix[6]arene.

It is reasonable to think that there is a competition between the association and the intermolecular interaction. When the calix[6]arene molecules associate with each other, the DMF molecule is extracted from the cave of calix[n]arenes, which results in the quenching of the second peak. With the further increasing of the concentration, the association is enhanced, which results in the first peak quenched.
3.4. Study of molecular recognition

From our experiment, it can be seen that the naphthalene and naphthoyl chloride have strong fluorescence. The addition of calix[n]arenes can not enhance the fluorescence of their DMF solution. However, after dealing with NaH, calix[n]arenes except p-tert butyl tetra-butoxy calix[4]arene can enhance the fluorescence of naphthoyl chloride greatly as shown in Fig. 5 but have little effect on the fluorescence of naphthalene. From the result, it can be proposed that the calix[n]arene can selectively recognize naphthoyl chloride in the presence of NaH, rather than in the absence of NaH. On the other hand, the fluorescence of naphthalene can not be enhanced by calix[n]arene no matter the presence of NaH or not, which indicates that there is no interaction between calix[n]arene and naphthalene.

In this paper, an equation of inclusion constant $k_n$ of the complex with one guest-multiple hosts has been deduced, the form of which is as follows:

$$\frac{1}{\Delta I_f} = \frac{1}{k_n x} \times \frac{1}{[H_0^n] + x}$$

In the equation, $\Delta I_f = I_{h-g} - I_{g} - I_{h}$, in which $I_{h-g}$, $I_g$, $I_h$ is the fluorescence intensity of the host–guest complex, the guest molecule and the host molecule, respectively. $[H_0^n]$ is the original concentration of the calix[n]arenes, $n$ is the host number in a complex and $x$ is a constant. By drawing the $1/\Delta I_f \sim 1/[H_0^n]$ graph, both the complex ratio and inclusion constant can be determined. If $n$ is just the actual host number of the complex, the $1/\Delta I_f \sim 1/[H_0^n]$ curve will be a line, else it will be a curve. From the intercept and the slope of the line, the inclusion constant can be obtained. From Fig. 6, it can be discovered that the inclusion constant $k_n$ is equal to $1.19 \times 10^4$ mol$^{-1}$l and $n = 1$, which indicates that the complex...
position ratio of the inclusion complex is 1:1 for calix[6]arene:guest.

4. Conclusion

At a high concentration, there is a self-association between calix[n]arene molecules, which can be determined by fluorescence. At the presence of NaH, calix[n]arenes that have hydroxyl can selectively complex with naphthoyl chloride and the host–guest ratio is 1:1.

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