

Study of the Complexation Behavior of Calixarene with Transition Metal Cations by UV-vis and Fluorescent Spectra

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A new fluorescent compound based on calix[4]arene skeleton was synthesized. Its complexation ability with transition metal ions, such as Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Ag^+ , was investigated by UV-vis and fluorescent spectra.

Keywords calixarene, transition metal cations, complexation

Calixarenes, emerging appeared after crown ethers and cyclodextrins as the third generation of host molecules, have proved to be useful as building-blocks or reactive platforms for assembling new receptors with various properties.^{1,2} Calixarene derivatives are able to bind selectively metal ions if their OH-groups on the lower rim are well modified.³ Many examples displayed that their high selectivity for the substrates was due to the accurate arrangement of binding sites in space. For instance, calixcrowns and calixarene podands (calixarene bearing amides, carboxylic acids or ketones) possess higher selectivity for alkali or alkaline earth metals.⁴ These ligands have been introduced with chromogenic or fluorescent groups and their recognition ability was investigated by the UV-vis or fluorescent spectra, in order to develop new chemical sensors.⁵ Main complexation research efforts have been focused on the "hard" metal ions; and some studies for "soft" metal ions, such as transition metal ions, have also been carried out. There have been wrought reviews to show how calixarene ligands can be as pre-organizing matrices for the construction of mononuclear or polynuclear transition metal complexes and also il-

lustrate their potential applications in catalysis and materials science.⁶ Most of articles reported the X-ray structure of transition metal complexes or solvent extraction properties, and there are a few studies on the complexation behavior by UV-vis and fluorescent spectra.⁷ Here we report a novel ligand based the skeleton of calix[4]arene **3**. It was found that the absorption and fluorescence spectra were markedly affected by some soft metal ion-bindings and not affected by hard metal ions.

Compound **3** was synthesized by the reaction of 8-hydroxyquinoline with **2** in the presence of K_2CO_3 (Scheme 1). The structure and cone conformation of compound **3** were confirmed by NMR, IR spectra, FAB-MS and elemental analyses.⁸

Fig. 1 displays changes in the absorption spectrum of the solution of **3** with the addition of $\text{Cu}(\text{ClO}_4)_2$ in a mixture solvent of chloroform-tetrahydrofuran (1/1, V/V) solution. The addition of $\text{Cu}(\text{ClO}_4)_2$ resulted in a decrease of the bands at 241 and 286 nm and an appearance of new bands around 255 and 340 nm with three isosbestic points at 245, 275 and 310 nm. $\text{Cu}(\text{ClO}_4)_2$ itself had no absorption at the regions of the new bands. The evidence suggests that the bathchromic effect was accompanied by the formation of a complex between **3** and Cu^{2+} .

Fig. 2 shows the changes in fluorescence emission of **3** with increasing the concentration of $\text{Cu}(\text{ClO}_4)_2$ from which, it can be seen, fluorescence of **3** could be efficiently quenched by Cu^{2+} .

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Scheme 1

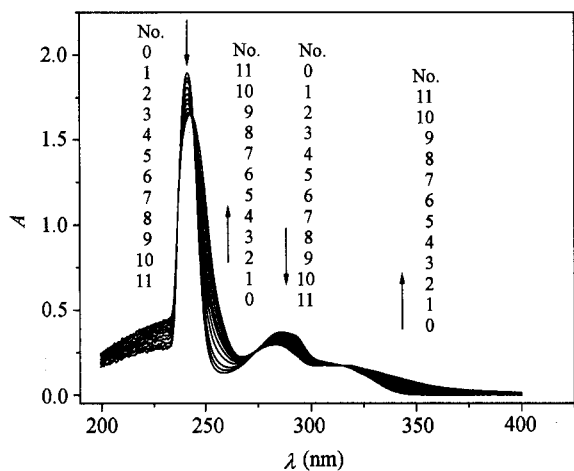
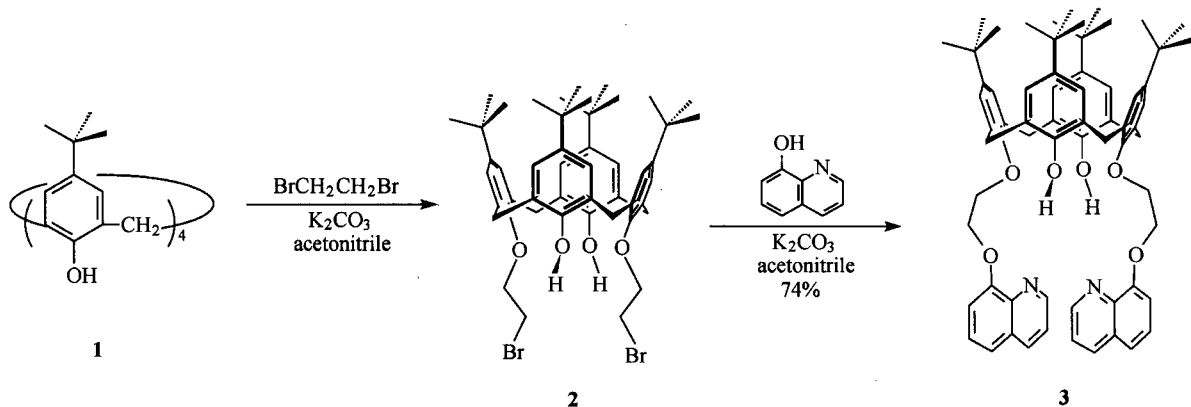


Fig. 1 Changes in the absorption spectrum of a chloroform-tetrahydrofuran (1:1, V/V) solution of calixarene **3** (2×10^{-5} mol/L) with the concentration of $\text{Cu}(\text{ClO}_4)_2$ increasing. The concentration of $\text{Cu}(\text{ClO}_4)_2$ ($\times 10^{-6}$ mol/L): (0) 0; (1) 0.83; (2) 2.50; (3) 4.16; (4) 5.82; (5) 7.48; (6) 9.13; (7) 11.61; (8) 14.08; (9) 16.53; (10) 18.99; (11) 21.43.

Similar measurements for several soft metal ions, such as Fe^{3+} , Co^{2+} , Ni^{2+} , Ag^+ and Al^{3+} , were examined. They displayed the same behavior as Cu^{2+} in the absorption spectra and the changes of fluorescence intensity.

Since $\text{Cu}(\text{ClO}_4)_2$ had no absorption at the excitation wavelength of 310 nm, the decrease of fluorescence intensity of **3** was not due to the absorption of $\text{Cu}(\text{ClO}_4)_2$. In order to exclude the possibility that heavy atoms lead to the decrease of fluorescence of **3**, the fluorescence of either **3** or the mixture of **3** and $\text{Cu}(\text{ClO}_4)_2$ were determined at 77 K. It is interesting that the intensity of fluorescence emission for both **3** and the mixture markedly increased

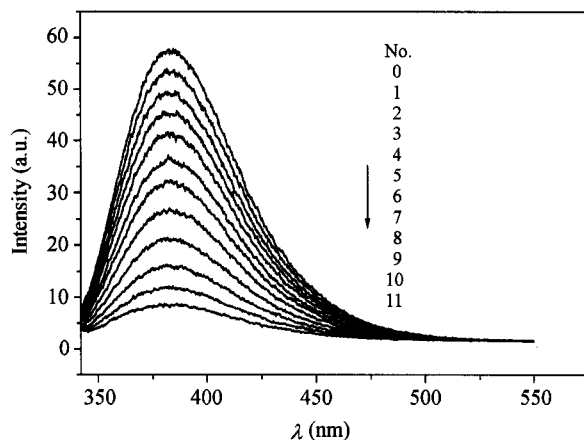


Fig. 2 Fluorescence of calixarene **3** (2×10^{-5} mol/L) quenched by $\text{Cu}(\text{ClO}_4)_2$ ($\lambda_{\text{ex}} = 310$ nm). The concentration of $\text{Cu}(\text{ClO}_4)_2$ ($\times 10^{-6}$ mol/L): (0) 0; (1) 0.83; (2) 2.50; (3) 4.16; (4) 5.82; (5) 7.48; (6) 9.13; (7) 11.61; (8) 14.08; (9) 16.53; (10) 18.99; (11) 21.43.

proportionally; and no phosphorescence was observed. By taking into account the results of both absorption and fluorescence spectra, the conclusion can be drawn that the fluorescence quenching was due to the formation of complexes and could be caused by the metal-ligand energy transfer between calixarene **3** and metal. ^1H NMR spectra of a mixture of **3** and $\text{Cu}(\text{ClO}_4)_2$ were determined in CDCl_3 . Two kinds of obvious proton shift were observed. One kind of protons came from the methylene in $-\text{OCH}_2\text{CH}_2\text{O}-$, while the other one could be assigned to the protons in quinoline group. These results can imply that the formation of these complexes between calixarene **3** and metal ions could be attributed to the coordination of functionalized group on the lower rim of calixarene.

Although the change in absorption spectra of **3** was similar upon adding Zn^{2+} or other transition metal ions, the fluorescence spectra of **3** showed different characteristic (Fig. 3) upon adding of Zn^{2+} other than Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ and Al^{3+} . The peak position of fluorescence spectra of **3** red shifted with increasing the concentration of Zn^{2+} and remained almost constant when the complex reaction between Zn^{2+} and **3** reached equilibrium. The peak position of fluorescence spectra of **3** red shifted for more than 30 nm in response to the complete complexation of Zn^{2+} as the ratio 1:1.

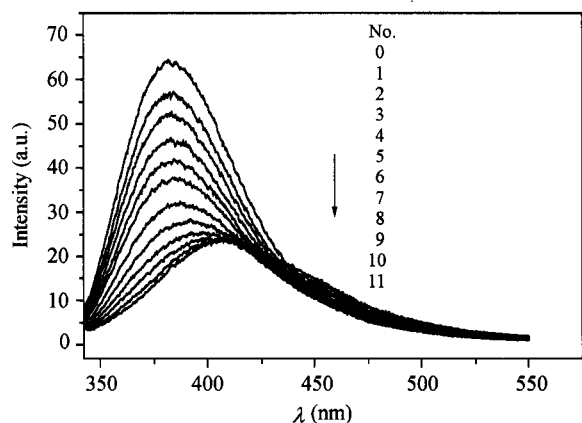


Fig. 3 Fluorescence spectra of calixarene **3** (2×10^{-5} mol/L) with the concentration increasing of $\text{Zn}(\text{ClO}_4)_2$ ($\lambda_{\text{ex}} = 310$ nm). The concentration of $\text{Zn}(\text{ClO}_4)_2$ ($\times 10^{-6}$ mol/L): (0) 0; (1) 2.51; (2) 4.18; (3) 6.68; (4) 10.02; (5) 12.53; (6) 16.70; (7) 20.62; (8) 24.68; (9) 28.72; (10) 34.35; (11) 40.73.

However, the changes in the fluorescence spectra could scarcely be detected when NaClO_4 or $\text{Mg}(\text{ClO}_4)_2$ were added into the solutions of **3**. And even where the amount of the Na^+ or Mg^{2+} was increased to hundreds of times of the concentration of **3**, the fluorescence of **3** could still not be quenched. So it can also be concluded that **3** could be as a good ligand for complexation Na^+ or Mg^{2+} .

From the fluorescence change with the concentration of $\text{Cu}(\text{ClO}_4)_2$, the stability constant between calixarene **3** and metal can be calculated.⁹ If a 1:1 complexing system is supposed to contain Cu^{2+} , calixarene **3** and the complex, Calix-Cu^{2+} , there can exist such relationship as

$$F/(F_0 - F) = 1/\{K_{\text{Calix-Cu}^{2+}}[\text{Cu}^{2+}]\}$$

where F is total intensity of the fluorescence, F_0 the initial intensity of the fluorescence, $K_{\text{Calix-Cu}^{2+}}$ the stability constant between **3** and Cu^{2+} . In Fig. 4, a linear plot of the mixture of **3** and Cu^{2+} by the use of change in the 380 nm fluorescence intensity is shown, this serves to confirm that the stoichiometry of complex should be 1:1. The stability constant was calculated from the plots with Equation. The stability constants of other soft metal ions with **3** were obtained in the same way. All the results are summarized in Table 1, from which no significant relationship can be found between K and the size of the metal ions. Therefore, it may be concluded that these soft metal ions would not enter the cavity of **3** in response to the complexation.

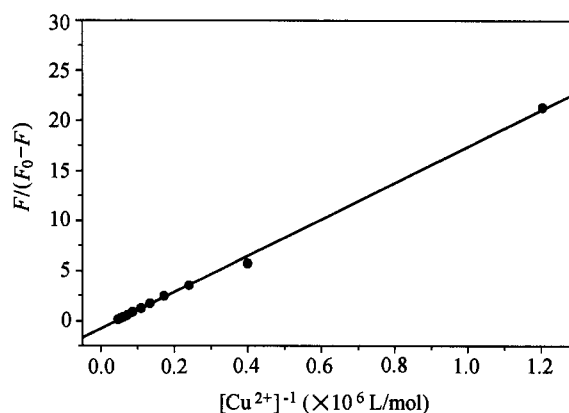


Fig. 4 Relative fluorescence intensity for a mixture of **3** and $\text{Cu}(\text{ClO}_4)_2$ plots against $1/[\text{Cu}(\text{ClO}_4)_2]$.

Table 1 Stability constants of metal ions as guests with calixarene **3** in solvent of chloroform-tetrahydrofuran (1:1, V/V) at room temperature.

Metal ions	Stability constants (log K)
Na^+	not detectable
Mg^{2+}	not detectable
Fe^{3+}	6.78 ± 0.18
Co^{2+}	4.70 ± 0.04
Ni^{2+}	4.06 ± 0.02
Cu^{2+}	5.48 ± 0.08
Zn^{2+}	5.01 ± 0.05
Ag^+	1.68 ± 0.04

In summary, a new fluorescent ligand based on calixarene has been found and its absorption and fluorescence spectra were markedly affected by some soft metal ion-bindings, which indicated that the formation of the

complexes in the solution.

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